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PART I.

Organic Chemistry

Preparation of Oxidation Products of Paraffin. I. ALFRED SCHAARSCHMIDT and MAX THIELE (*Ber.*, 1920, **53**, [*B*], 2128—2143).—The process depends on the chlorination of paraffin, and subsequent elimination of hydrogen chloride, yielding an olefine, which is oxidised to a fatty acid.

Chlorine is passed into paraffin at 160°, the apparatus being so arranged that the current of gas is broken up by a Witt's stirrer; the gas is almost completely utilised, and the operation, which proceeds without the aid of external heating, is interrupted when the required gain in weight has been attained. Chlorination does not occur quite uniformly, and, in addition to isomeric monochloro-derivatives, dichloro-products are also formed before all the paraffin is attacked. The chlorine can be quantitatively removed as hydrogen chloride by heating the chloro-paraffins at about 300°, but since the products obtained in this manner have a decidedly lower iodine number than those prepared by the aid of alcoholic potassium hydroxide at a lower temperature, the latter only have been used for purposes of oxidation. For the latter process, potassium permanganate was initially employed; thus the silver salt of an acid, $C_{14}H_{29}\cdot CO_2H$, was isolated from an olefine which had the bromine number 20·4 (obtained from a chloro-paraffin with 10·6% of chlorine by treatment with alcoholic potassium hydroxide solution). The less saturated olefines absorb oxygen far more rapidly and to a much greater extent. Since the oxidisability of these unsaturated hydrocarbons, which are insoluble in

water, depends greatly on their state of division, the following modifications of the procedure were adopted with an olefine obtained from a chloro-paraffin with 32% of chlorine: (i) the olefine is emulsified in a solution of sodium palmitate and treated with aqueous potassium permanganate; the latter is rapidly reduced, and action is complete when the weight of the permanganate used is about six times that of the olefine; (ii) since fatty acids, and therefore soaps, are produced by the oxidation, the reaction is started with a small quantity of sodium palmitate and olefine, and further additions of the latter are made in proportion as the potassium permanganate is reduced. The amount of crude acid formed is about the same in either case, as is also the proportion of fatty acid and unsaponifiable matter; the acid number of the products obtained by the second process is greater than that of those obtained in the first. Oxidation by permanganate does not lead solely to rupture at the double bond, but also affects the initial fission products. Also, when a considerable number of double bonds are present in the olefine, considerable amounts of acids are formed, which are soluble in water, and thus remain in the mother liquor when the solutions are acidified, whilst also much of the olefine is oxidised to carbon dioxide.

The action of ozone on the olefines has also been investigated, the addition of the gas taking place readily at about 40° in the absence of solvent. The amount of ozone absorbed corresponds approximately with the quantity of hydrogen chloride which is eliminated during the formation of the olefine. Fission of the ozonide is effected with water, and the non-acidic, aldehydic portion is subsequently oxidised by ozone. One hundred and fifty grams of olefine (from a chloro-paraffin with 19·4% of chlorine and alcoholic potassium hydroxide solution) gave 105 grams of higher fatty acids and considerable amounts of lower fatty acids soluble in water. H. W.

The Oxidation of Aliphatic Hydrocarbons by Nitrogen Peroxide. CH. GRÄNACHER (*Helv. Chim. Acta*, 1920, **3**, 721—737).—In a review of the subject of the oxidation of paraffins to aliphatic acids, the author points out that until very recent times (compare Kelber, A., 1920, i, 280; Franck, *ibid.*, i, 417; and Grün, *ibid.*, i, 518) the various processes described have either been too vigorous, such as the early use of nitric acid, or too slow and incomplete, such as the passage of air into the hot oils. The present experiments, carried out before Kelber's work was announced, were based on the idea of combining the above extreme processes by submitting the heated oil to a current of air containing 2% of nitrogen peroxide. It was found that in the case of a paraffin-wax with m. p. 50—52°, oxidation to substances soluble in aqueous sodium hydroxide required ten, seven, six, and four days, respectively, at 110°, 120°, 135°, and 150°. The products were not discoloured, and consisted of a mixture of acetic, butyric, and higher fatty acids, with about 15% of insoluble material.

The appearance of nitrogen peroxide in the waste gases led to

an inquiry as to its rôle in the oxidation. Experiments with pure nitrogen peroxide were therefore carried out at 140°, and it was found that the gas was rapidly absorbed and the oxidation completed in eight to ten hours. The colourless gas which was evolved contained carbon dioxide and a little hydrogen cyanide, but was chiefly nitric oxide. The idea of making use of nitrogen peroxide merely as a catalyst would not be practicable, however, owing to losses in the form of nitrogen gas, hydrogen cyanide, and, presumably, nitro-compounds, which impart a red colour to the alkaline solutions of the products.

With the purpose of studying the mechanism of the oxidation, pure *n*-undecane was obtained by reducing methyl nonyl ketone (from oil of rue) by means of amalgamated zinc and hydrochloric acid, and treated with pure nitrogen peroxide at 140° for ten hours. The gaseous products were about the same as before, but quite 40% of the hydrocarbon was left unchanged. The oxidation products consisted of the lower acids, but no acid of higher molecular weight than nonoic acid could be found. It follows, therefore, that this method is not designed to furnish any definite acid from a particular paraffin hydrocarbon, and also that the higher paraffins in nature must consist to only a small extent of normal hydrocarbons. J. C. W.

Oxidation of Paraffin Wax to True Wax in Ultra-violet Light. AD. GRÜN and TH. WIRTH (*Zeitsch. angew. Chem.*, 1920, **33**, 291—292).—Parallel experiments on the oxidation of paraffin wax to waxes containing esters were made with and without the use of ultra-violet light. The paraffin wax was heated at 160° in a current of air for three or five and a-half hours, and the resulting vapours condensed and collected in receivers immersed in ice. The oxidation in the absence of ultra-violet light proceeded somewhat further, but the amount of solid material left in the reaction tube was about the same in each case. Hence ultra-violet light appears to have practically no influence on the oxidation of paraffin wax. C. A. M.

Methyl Chloride. T. YONEYAMA and J. BAN (Jap. Pat., 35701, 1920).—Methyl chloride is easily prepared without explosion by passing dry methane and chlorine over a catalyst composed of a mixture of animal charcoal and finely divided calcium oxide at 250°, at the rate of 3 and 5·5 litres per minute respectively.

CHEMICAL ABSTRACTS.

Preparation of Ethyl Iodide. BEATRICE ELIZABETHA HUNT (T., 1920, **117**, 1592—1594).

Intersolubility of Chloropicrin and Water. THOS. G. THOMPSON and JOHN H. BLACK (*J. Ind. Eng. Chem.*, 1920, **12**, 1066—1067).—The solubility of chloropicrin in water at temperatures of 0°, 25°, and 75° was determined by estimating the amount dissolved by the aqueous layer separating from an emulsion main-

tained at the respective temperatures. The following results were obtained: at 0° 0·2272 gram, at 25° 0·1621 gram, and at 75° 0·1141 gram per 100 c.c. The solubility of water in chloropicrin was 0·2265 gram at 55°, 0·1243 gram at 41°, and 0·1003 gram at 32°. These results are plotted in solubility curves. [See, further, *J. Soc. Chem. Ind.*, 1920, 831A.] C. A. M.

Catalytic Dehydration of Amyl Alcohol from Fermentation. J. B. SENDERENS (*Compt. rend.*, 1920, **171**, 916—919).—When fermentation amyl alcohol is dehydrated by passing its vapour over aluminium silicate at 340—350°, the product being collected in three separate fractions, the three components of each fraction are β-methyl-Δ^{β}-butene, β-methyl-Δ^{α}-butene, and γ-methyl-Δ^{α}-butene. The relative proportions of these three hydrocarbons are: in fraction (1) 704:180:25, in fraction (2) 595:238:65, and in fraction (3) 302:392:182 by volume, there being thus a considerable change in the relative proportions of the isomerides as the catalyst ages. This change is explained on the basis that the β-methyl-Δ^{β}-butene is obtained by an isomeric change of β-methyl-Δ^{α}-butene under the influence of the catalyst, and that this change diminishes as the catalyst becomes less active. W. G.

The Montan Wax of the Central German Coal. R. PSCHORR and J. K. PFAFF (*Ber.*, 1920, **53**, [*B*], 2147—2162).—The wax has been investigated more particularly with the object of elucidating the nature of the alcohols present, and *tetracosanol*, $C_{24}H_{50}O$, ceryl alcohol, and myricyl alcohol have been definitely identified.

The crude, crushed wax was successively extracted with ether and acetone until almost colourless solutions were obtained, and was thereby divided into a viscid, brown resin, a powdery, brown mass, and a fine, greyish-brown residue, which were separately examined; the analytical constants showed that the main portion of the free acid is present in the extracts, particularly in the second. The products were hydrolysed with alcoholic potassium hydroxide in the presence of benzene, the potassium salts were converted into the calcium salts, and the latter exhaustively extracted with acetone, thereby yielding solutions of the free alcohols and unsaponifiable matter. Separation of the latter was effected by treatment with acetic anhydride and crystallisation of the acetates from alcohol, in which they are much more readily soluble than the unsaponifiable matter. The individual acetates were subsequently separated from one another by crystallisation from a mixture of equal volumes of alcohol and ether, whereby *tetracosanyl acetate*, m. p. 59°, ceryl acetate, m. p. 65°, and myricyl acetate, m. p. 70°, were obtained; hydrolysis of the acetates with alcoholic potassium hydroxide gave the pure alcohols, m. p.'s 83°, 79°, and 88° respectively. The ethereal extract yielded mainly tetracosanol and ceryl alcohol, whilst the latter was obtained in an almost pure condition from the acetone extract.

The calcium salt (see above) was decomposed with concentrated hydrochloric acid and benzene, and the liberated montanic acid separated from resin and humic acids by conversion into its methyl ester, m. p. 66·5°, by methyl alcohol and sulphuric acid or hydrogen chloride, from which it was recovered (m. p. 83·5°) by acid hydrolysis. Its isolation was effected most readily from the acetone extract.

Analysis shows the ethereal extract to contain 26% of free acid (reckoned as montanic acid), 41·8% of montanic ester, and 32·2% of substances of unknown composition; the corresponding figures for the acetone extract are 51·3%, 46·5%, and 2·2%, and for the residue 0%, 63·5%, and 36·5%. The specimen of wax contains, therefore, at most 17% of montanic acid, 53% of montanic esters, and at least 30% of substances of unknown composition.

In some preliminary experiments, the montan resin was isolated from the ethereal extract; its alkaline solution, when slowly evaporated, deposited small amounts of an unsaturated, neutral, crystalline substance, $C_{24}H_{34}O_2$, m. p. 241°; the amount of material was insufficient for an extended examination, but it is shown that the substance is not an ester. H. W.

The Action of the Grignard Reagent on Thiocyanates. ROGER ADAMS, H. B. BRAMLET, and F. H. TENDICK (*J. Amer. Chem. Soc.*, 1920, **42**, 2369—2374).—Alkyl thiocyanates (1 mol.) react with Grignard's reagent (3 mols.) to give a mixture of thio-ether and mercaptan. If the thiocyanate is added to the Grignard reagent, the yield of mercaptan is higher and of thio-ether is lower than if the Grignard reagent is added to the thiocyanate. If an aromatic Grignard reagent is used, the second reaction, formation of mercaptan, is the principal one, almost to the exclusion of the first, formation of thio-ether. When magnesium phenyl bromide is used, the nitrile formed as a subsidiary product of the second reaction, $RSCN + RMgBr \longrightarrow RCN + RSMgBr \longrightarrow RSH$, reacts with the excess of Grignard reagent to give an additive product, which, on decomposition, yields a ketone.

*iso*Amyl thiocyanate gives with magnesium ethyl bromide ethyl *iso*amyl sulphide, b. p. 158—161°, and *iso*amyl mercaptan, b. p. 120—122°; with magnesium propyl bromide it gives *propyl* iso*amyl sulphide*, b. p. 179—181°/740 mm., D^{20} 0·851, n_D^{20} 1·4495, and *iso*amyl mercaptan; with magnesium phenyl bromide it gives benzophenoneimide, isolated as its hydrochloride, and small amounts of *phenyl* iso*amyl sulphide* and *iso*amyl mercaptan.

*iso*Butyl thiocyanate gives with magnesium ethyl bromide ethyl *iso*butyl sulphide and *iso*butyl mercaptan.

Heptyl thiocyanate with magnesium ethyl bromide gives *ethyl heptyl sulphide*, b. p. 188—192°/732 mm., D^{20} 0·871, n_D^{20} 1·4518, and heptyl mercaptan, b. p. 174—176°.

Benzyl thiocyanate gives with magnesium ethyl bromide benzyl ethyl sulphide, b. p. 218—220°, and benzyl mercaptan, b. p. 194—195°; with magnesium *iso*butyl bromide, *benzyl* iso*butyl*

sulphide, b. p. 243—244°, D^{20} 0·968, n_D^{20} 1·4912, and benzyl mercaptan; with magnesium phenyl bromide, benzophenoneimide, isolated as its hydrochloride.

Benzoyl cyanide (1 mol.) reacts with magnesium phenyl bromide (2 mols.) to give triphenylcarbinol, triphenylmethane, and benzoic acid. If the reagents are in equimolecular proportions, the products are triphenylacetonitrile, benzophenone, and benzoic acid.

Dimethyloxanilide with excess of the Grignard reagent yields phenylmethylamides of α-ketonic acids, the following of which were prepared: *methylanilide* of *α-ketobutyric acid*, b. p. 165°/17 mm.; *methylanilide* of *pyruvic acid*, m. p. 83—84°; and *methylanilide* of p-*toluoylformic acid*, m. p. 128—129°. W. G.

Reaction between Selenium Monochloride and Ethylene. F. H. HEATH and WALDO L. SEMON (*J. Ind. Eng. Chem.*, 1920, **12**, 1100—1101).—Pure selenium monochloride was prepared by dissolving selenium in 30% fuming sulphuric acid, and gently heating the flask, through which was passed a current of dry hydrogen chloride. The crude distillate was purified by shaking it with successive quantities of fuming sulphuric acid until the acid layer no longer showed the green coloration of selenium sulphite, and then allowing it to remain over dry sodium chloride for a week. On passing a slow current of ethylene into selenium monochloride, selenium was precipitated and hydrogen chloride evolved. After completion of the reaction, chloroform was added, and the liquid filtered. White, needle-shaped crystals (m. p. 118°, decomp.) separated, and when recrystallised from chloroform had the composition $C_4H_6Cl_4Se$. The compound was found to be s-*tetrachlorodiethyl selenide* (compare Bauser, Gibson, and Pope, T., 1920, **117**, 1453). C. A. M.

The Preparation of Dichloroacetic Acid from Chloral. GEORGE W. PUCHER (*J. Amer. Chem. Soc.*, 1920, **42**, 2251—2259). —Dichloroacetic acid may be prepared on a large scale by adding 400 grams of commercial sodium cyanide dissolved in 1100 c.c. of water to a solution of 1 kilo. of chloral hydrate in 3000 c.c. of water at 40°, with constant stirring. The addition should be at such a rate that the temperature does not rise above 50°. The water is evaporated off after one hour, the crude sodium salt is suspended in benzene, and dry hydrogen chloride is passed into the ice-cold solution. The sodium chloride is filtered off, and the dichloroacetic acid is recovered from the filtrate. Small-scale experiments confirm Kötz's view as to the mechanism of the reaction (A., 1914, i, 186).

If dichloroacetic acid is slowly added to sodium ethoxide in absolute alcohol, it yields *sodium diethoxyacetate*, and if, after the alcohol has been distilled off, methyl sulphate is added to this salt and the mixture is heated on a water-bath for three hours, *methyl diethoxyacetate*, $CH(OEt)_2{\cdot}CO_2Me$, b. p. 184—185°, D^{25} 1·0049, is obtained. W. G.

The Position of the Double Bond in Ricinoleic Acid. KARL STOSIUS and KARL WIESLER (*Biochem. Zeitsch.*, 1920, **111**, 1—8).—On oxidising ricinoleic acid with an alkaline solution of potassium permanganate, a mixture of azelaic and suberic acids was obtained. By neutralising the mixture with a known amount of sodium hydroxide and then adding in succession one-fourth of the requisite hydrochloric acid necessary to liberate the free acids, and extracting each fraction with ether, azelaic acid, m. p. 106°, was obtained in the first fraction, and suberic acid, m. p. 140°, in the last fraction. Fractions two and three contained a mixture of both. It is suggested that azelaic and suberic acids are formed by the oxidation of two different isomeric ricinoleic acids, the probable explanation of the presence of the second isomeride being that the alkali hydroxide causes a shifting of the position of the double linking in a portion of the ricinoleic acid, this being nearer by one carbon atom to the carboxyl group. S. S. Z.

The C_4-Saccharinic Acids. I. The Resolution of *dl*-$\beta\gamma$-Dihydroxybutyric Acid into the Optically Active Components. The Derivatives of these Acids. J. W. E. GLATTFELD and GEORGE E. MILLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2314—2321).—*dl*-$\beta\gamma$-Dihydroxybutyric acid was resolved into its two optically active components by passage through its brucine salt. 1-$\beta\gamma$-*Dihydroxybutyric acid* has $[\alpha]_D$ $-8{\cdot}29°$, and gives a *brucine* salt, $[\alpha]_D^{20}$ $-29{\cdot}42°$, a *barium* salt, $[\alpha]_D^{20}$ $+1{\cdot}48°$, a *calcium* salt, $[\alpha]_D^{20}$ $+2{\cdot}47°$, and a *phenylhydrazide*, m. p. 102—103°, $[\alpha]_D$ $+1{\cdot}71°$. The d-*acid* has $[\alpha]_D$ $+8{\cdot}00°$, and gives a *brucine* salt and a *barium* salt, $[\alpha]_D$ $-1{\cdot}48°$.

$CH_2{\cdot}OH$	$CH_2{\cdot}OH$
|	|
$HO{\cdot}C{\cdot}H$	$H{\cdot}C{\cdot}OH$
|	|
$H{\cdot}C{\cdot}H$	$H{\cdot}C{\cdot}H$
|	|
CO_2H	CO_2H
l-Acid.	*d*-Acid.

From their behaviour on oxidation, the configurations of the two acids must be as in the annexed formulæ. W. G.

The Rotatory Power of Tartaric and Malic Acids in Solution. R. DE MALLEMANN (*Compt. rend.*, 1920, **171**, 950—952). —In benzene–alcohol solution, *d*-tartaric acid gives a lævorotation for all the rays from $\lambda = 0{\cdot}578$—$0{\cdot}436\,\mu$, the dispersion being normal, $[\alpha]_{436}/[\alpha]_{578} = 4{\cdot}45$ at 21°. In the presence of neutral salts of strong acids, in particular in the presence of calcium chloride, the dextrorotation of tartaric acid in aqueous solution diminishes and becomes an increasing lævorotation as the concentration of the calcium chloride increases. The dispersion, which is at first abnormal, becomes normal by the addition of a suitable amount of calcium chloride.

The addition of benzene to an alcoholic solution of *l*-malic acid results in a dextrorotatory solution. Similarly, the addition of calcium chloride to an aqueous solution of malic acid gives a more highly dextrorotatory solution. W. G.

Colloids Soluble in Water from Artificial Charcoals. K. A. HOFMANN and WILHELM FREYER (*Ber.*, 1920, **53**, [*B*], 2078—2095. Compare A., 1913, ii, 954).—Colloidal substances of an acid character have been obtained by oxidising charcoal under certain conditions. For the successful preparation of these substances, it was found necessary to use soot or charcoal prepared at a low temperature; the behaviour of the charcoal towards oxidising agents was found not to depend on the nature of the material from which it was prepared, but on the temperature to which it had been subjected. The materials used in the experiments were (*a*) soot, prepared by burning different hydrocarbon flames against a water-cooled surface in a limited supply of air, and then heating the product for two hours at 300°; (*b*) charcoal, prepared by heating sawdust gradually to 600°. The colloidal oxidation products were best prepared by gradually adding potassium chlorate to a suspension of the soot or charcoal in 15% aqueous hydrochloric acid. Part of the product was soluble in water (water-soluble colloid), precipitated by acid, and another portion was soluble in dilute alkali (alkali-soluble colloid). The latter is reprecipitated by alkali hydroxide, carbonate, or hydrogen carbonate greater than 1% in strength. The water-soluble colloid is a higher oxidation product than the alkali-soluble. They are black, and form intensely coloured solutions.

Alkali-soluble colloid from soot, $(C_{12}HO_2)_n$.

Water-soluble colloid from soot, $C_{11}H_3O_4$. It forms an ammonium salt, $(C_{11}H_2O_4NH_4)_n$, in the form of shining, black hairs, and an insoluble barium salt, $[(C_{11}H_6O_6)_2Ba]_n$, by precipitation of a solution of the ammonium salt with barium chloride.

Alkali-soluble colloid from charcoal, $(C_{14}H_7O_7)_n$. This contains two carboxyl groups, forming a secondary ammonium salt, $C_{14}H_7O_8(NH_4)_2$, a barium salt, $C_{14}H_9O_9Ba$, and a calcium salt containing more water, $C_{14}H_{13}O_{11}Ca$.

Water-soluble colloid from charcoal, $(C_{14}H_7O_8)_n$. This colloid forms adsorption products with salts of the alkaline earths.

From their behaviour with hydrazine hydrate, it is probable that the above products contain, besides carboxyl groups, reactive carbonyl groups. Their colour intensity in solution is of the same order as that of dyes of high molecular weight. Viewed with the ultramicroscope, the solutions show submicrons with well-marked Brownian movement, the dimensions being, for the alkali-soluble particles, $3—4 \times 10^{-6}$, and for the water-soluble, $1·7—2 \times 10^{-6}$ cm. The precipitation of the colloidal particles, which are negatively charged, by a number of salts was studied. The colloids adsorb iodine, methylene-blue, and bacteria. E. H. R.

A Sulphide Acid: Butyl Ether of Thioglycollic Acid [Butylthiolacetic Acid]. YOSHISUKE UYEDA and E. EMMET REID (*J. Amer. Chem. Soc.*, 1920, **42**, 2385—2389).—Sodium chloroacetate readily reacts in aqueous solution with the sodium salt of butyl mercaptan to give n-*butylthiolacetic acid*,

$$C_4H_9·S·CH_2·CO_2H,$$

b. p. 140°/10 mm., D_0^0 1·0771, D_{25}^{25} 1·0631, n_D^{25} 1·4780. This acid gave crystalline *barium*, *calcium*, *strontium*, *nickel*, *cobalt*, *zinc*, *cadmium*, *manganese*, *copper*, and *silver* salts. The *ammonium* salt was unstable, and the *magnesium* and *lead* salts were not crystalline. It gave a *chloride*, b. p. 218° (corr.)/758 mm., D_{25}^{25} 1·0956, n_D^{25} 1·4810; an *amide*, m. p. 65°; a *methyl* ester, b. p. 85°/10 mm., D_0^0 1·0299, D_{25}^{25} 1·0125, n_D^{25} 1·4590; an *ethyl* ester, b. p. 89—90°/10 mm. D_0^0 1·0044, D_{25}^{25} 0·9881, n_D^{25} 1·4560; a *propyl* ester, b. p. 93—94°/6 mm., D_0^0 0·9892, D_{25}^{25} 0·9723, n_D^{25} 1·4555; a *butyl* ester, b. p. 105—106°/6 mm., D_0^0 0·9794, D_{25}^{25} 0·9630, n_D^{25} 1·4555; a p-*nitrobenzyl* ester, and a p-*bromophenacyl* ester, m. p. 95°.

W. G

Modified Method for the Preparation of α-Sulphocarboxylic Acids. H. J. Backer and J. V. Dubský (*Rec. trav. chim.*, 1920, **39**, 694—698).—A more detailed account of work already published (A., 1920, i, 288). W. G.

α-Sulphopropionic Acid and its Acid Salts. A. P. N. Franchimont and H. J. Backer (*Rec. trav. chim.*, 1920, **39**, 689—693. Compare A., 1915, i, 55).—The free acid behaves as a strong acid, but its acid salts behave as weak organic acids, and it is probable that in these salts it is the hydrogen of the sulphonic group which has been replaced by metals or organic bases. The *aniline hydrogen* salt has m. p. 163°, and the *α-naphthylamine hydrogen* salt has m. p. 233°. W. G.

Sulphoxyl Compounds. XII. Action of Oxidising Agents on Formaldehyde Sulphoxylate. A. Binz and E. Haberland (*Ber.*, 1920, **53**, [*B*], 2030—2034).—The action of formaldehyde sulphoxylate on mercuric chloride has been investigated, since neosalvarsan (the product of the condensation of salvarsan and formaldehyde sulphoxylate) is administered in conjunction with mercuric chloride; it leads to the formation of formaldehyde bisulphite and mercurous chloride, or mercury if the sulphoxylate is present in excess, whilst, also, to a minor extent, the latter is decomposed by the liberated hydrochloric acid, with precipitation of sulphur, before the action with mercuric chloride has attained completion. Alkaline thiosulphate solution oxidises formaldehyde sulphoxylate in accordance with the equation

$$OH\cdot CH_2\cdot O\cdot SONa + Na_2S_2O_3 + 2NaOH = OH\cdot CH_2\cdot O\cdot SO_2Na + Na_2SO_3 + Na_2S + H_2O,$$

the reaction thus being analogous to that occurring between hyposulphite and thiosulphate (Binz and Sondag, A., 1906, ii, 23).

H. W.

Volatile Oil of *Artemisia annua*, L. II. The Constitution of Artemisia Ketone. Yasuhiko Asahina and Seisi Takagi (*Yakugaku Zasshi* [*J. Pharm. Soc. Japan*], 1920, No. 464, 837—864. Compare A., 1918, i, 76).—On oxidation with potassium dichromate and sulphuric acid, or concentrated nitric

acid, tetrahydroartemisia ketone gives $\alpha\alpha$-dimethylbutyric acid (confirmed as its anilide, m. p. 91—92°), whilst with potassium permanganate artemisia ketone gives dimethylmalonic acid. In preparing artemisia ketone semicarbazone, a new ketone, $C_{10}H_{16}O$, isomeric with artemisia ketone, was isolated as its *semicarbazine* compound, m. p. 70—72°, anhydride, m. p. 103—104°, which, by the action of nitrous acid, was converted to an *azide*, m. p. 162°; this, when boiled with potassium hydroxide, yielded the free ketone. The new ketone gives tetrahydro-artemisia ketone by reducing with hydrogen in the presence of platinum-black, is therefore considered to be an $\alpha\beta$-unsaturated compound, and named iso*artemisia ketone*, b. p. 182—183°, D_4^{17} 0·8711, n_D^{17} 1·46880. By the action of hydroxylamine, the *iso*-compound yields two compounds, *hydroxylaminodihydro*iso*artemisia ketoxime*, m. p. 170°, and *hydroxylaminodihydro*iso*artemisia ketone*, m. p. 162°. The latter forms a true nitroso-compound, *nitrosodihydroartemisia ketone*, m. p. 64°, by oxidation with mercuric oxide, which shows that the nitroso-group has displaced the tertiary hydrogen atom. The authors suggest the following constitutions for artemisia ketone (I) and *iso*artemisia ketone (II) respectively: (I) $CH_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CMe{:}CH_2$; (II) $CH_2{:}CH{\cdot}CMe_2{\cdot}CO{\cdot}CH{:}CMe_2$. K. K.

Mutarotation of Dextrose in Solutions of Secondary Sodium Phosphate. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1920, **110**, 181—192).—Like sodium carbonate, disodium phosphate accelerates the mutarotation of dextrose in aqueous solution. The accelerating influence depends on the concentration of the salt. Dextrose is more susceptible to the action of sodium carbonate than to that of disodium phosphate. S. S. Z.

Allyl-β-glucoside. EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1919, **108**, 3—8. Compare A., 1912, i, 884; Bourquelot and Bridel, A., 1912, i, 790).—Allylglucoside tetra-acetate,

$$C_3H_5{\cdot}O{\cdot}C_6H_7O_5Ac_4,$$

prepared by treating acetobromoglucose with allyl alcohol in the presence of silver carbonate, has $[\alpha]_D^{17}$ $-26{\cdot}21°$ to $-26{\cdot}36°$, m. p. 89—90°. Allylglucoside, $C_3H_5{\cdot}O{\cdot}C_6H_{11}O_5$, obtained by hydrolysing the tetra-acetate with baryta, has $[\alpha]_D^{17}$ $-40{\cdot}25°$ to $-40{\cdot}48°$, m. p. 102—103°. On brominating the tetra-acetate in chloroform, allylglucoside tetra-acetate dibromide, $C_3H_5Br_2{\cdot}O{\cdot}C_6H_7O_5Ac_4$, is obtained having $[\alpha]_D^{17}$ $-10{\cdot}54°$, m. p. 91—93°. The bromoallyl-β-glucoside, $C_3H_4Br{\cdot}O{\cdot}C_6H_{11}O_5$, was prepared by hydrolysing the dibromide with baryta, and has $[\alpha]_D^{17}-49{\cdot}72°$, m. p. 127—128° (corr.). S. S. Z.

Two Isomeric Chlorotetra-acetyl-*d*-fructoses. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 342—346).—By the action of phosphorus pentachloride on β-tetra-acetylfructose dissolved in dry chloroform at low temperatures, two isomeric chloro-derivatives are formed. The first,

α-chlorotetra-acetyl-*d*-fructose, which is formed when the reaction is carried out in presence of anhydrous aluminium chloride, is highly unstable, and can only be purified by recrystallising from dry ether at 0°. It has m. p. 83° and $[\alpha]_D^{20}$ $-160\cdot9°$, the maximum value in chloroform solution. From ether it crystallises in small, colourless, transparent needles, elongated in the direction of the *c*-axis, belonging to the rhombic (probably bisphenoidal) system, $a : b : c = 0\cdot9759 : 1 : 0\cdot3284$. The isomeric β-chlorotetra-acetyl-*d*-fructose, which is formed when the reaction is carried out without a catalyst, is less unstable than the α-form, although it gradually decomposes when repeatedly recrystallised. In taste it is much less bitter than the α-form. It is best recrystallised from hot alcohol, and has m. p. 108°, $[\alpha]_D^{20}$ $+45\cdot2°$ in chloroform. Its benzene solution deposits large, transparent, prismatic crystals, rhombic bisphenoidal, $a:b:c = 1\cdot7478:1:0\cdot7112$. There is a certain similarity in form development between the crystals of the two isomerides, but this similarity is not so close as in the case of α- and β-penta-acetyl-*d*-fructoses (A., 1918, i, 6). E. H. R.

Solubility of Lactose. J. Gillis (*Rec. trav. chim.*, 1920, **39**, 677—678).—The author has redetermined the solubility of lactose in water over the temperature range 50—100°. The results confirm those previously published (A., 1920, i, 217). W. G.

Catalytic Combustion of Sucrose. L. Brandt (*Chem. Zeit.*, 1920, **44**, 881—882).—When an ordinary lump of sugar is moistened at one corner with a trace of blood, milk, etc., and then lighted, it burns readily; traces of certain mineral substances also accelerate the rate of combustion, whilst others are without effect, but there seems to be no general explanation as to why a substance should or should not aid the combustion. W. P. S.

Studies in Fermentation. V. Enzyme Formation through the Action of Ions. W. Biedermann (*Fermentforsch.*, 1920, **4**, 1—28; from *Chem. Zentr.*, 1920, iii, 638—639. Compare A., 1920, i, 15).—I. *Amylose, Amylopectin, and Amylocellulose.*—A clear amylose solution can be obtained by extracting wheaten starch with water at 80°. The extracted residue the author considers to be "amylopectin." An amylose solution could not be obtained at the ordinary temperature from potato starch. The extracted residues from wheaten and pea starch, on being digested with filtered saliva, left a residue, which did not give the iodine reaction and behaved like cellulose. Potato does not contain this substance.

II. *The Influence of Salts on the Autolytic Cleavage of Pure Amylose.*—From the results the author obtained by studying the action of various salts on soluble amylose, he concludes that the soluble amylose forms a complex with certain ions which acts as an autolytic enzyme. Amylopectin is resistant to the action of saliva in the presence of those salts, and can therefore be separated

from it in this way. It also is evident that the autolytic enzyme formed is not identical with the saliva enzyme (ptyalin ?).

S. S. Z.

Constitution of Polysaccharides. I. The Relationship of Inulin to Fructose. JAMES COLQUHOUN IRVINE and ETTIE STEWART STEELE (T., 1920, **117**, 1474—1489).

The Constitution of Polysaccharides. II. The Conversion of Cellulose into Glucose. JAMES COLQUHOUN IRVINE and CHARLES WILLIAM SOUTAR (T., 1920, **117**, 1489—1500).

Constitution of Cellulose. KURT HESS (*Helv. Chim. Acta*, 1920, **3**, 866—869. Compare A., 1920, i, 532).—A reply to criticisms by Karrer (A., 1920, i, 620). Hess regards cellulose as a complex of "celluxose" ("hydrocellulose") systems, held together by virtue of the residual affinities of the hydroxyl groups, the components themselves having definite chemical structure, being, in fact, tannin-like units derived from dextrose. Karrer, on the other hand, sees in the relationship of a simple cellulose or starch molecule to the whole fibre or grain something akin to the relationship between a single molecule and a rigid crystal.

Attention is directed to the fact that copper is the only heavy metal which gives ammine-hydroxides capable of dissolving cellulose. Ammoniacal nickel oxide, and bases such as $[Co\,en_3](OH)_3$, $\left[Co\begin{array}{c}en_2\\OH_2\\OH\end{array}\right](OH)_2$, and $\left[Co\begin{array}{c}en_2\\OH_2\\OH_2\end{array}\right](OH)_3$, are quite inactive, from which the conclusion is drawn that the copper complexes must be very different in structure.

J. C. W.

Synthesis of a Tetrasaccharide containing Sulphur. FRITZ WREDE (*Zeitsch. physiol. Chem.*, 1919, **108**, 115—119).—The *tetradeca-acetate* of *dicellosyl sulphide*, $C_{52}H_{70}O_{34}S$, m. p. 262° (uncorr.), was prepared by treating acetobromocellose with alcoholic potassium sulphide. The tetrasaccharide, *dicellosyl sulphide*, $C_{24}H_{42}O_{20}S$, was obtained from the acetyl derivative by saturating a methyl-alcoholic solution of it with ammonia, evaporating in a vacuum, and extracting with hot 90% alcohol; it has $[\alpha]_D^{16}$ $-48{\cdot}33°$. The *potassium* compound of the tetrasaccharide, $C_{24}H_{40}O_{20}SK_2,4H_2O$, m. p. 170—180°, was obtained by treating the acetyl derivative with aqueous-alcoholic potassium hydroxide in hot alcohol.

S. S. Z.

The Physical Structure of some Organic Compounds of High Molecular Weight. I. R. O. HERZOG and WILLI JANCKE (*Ber.*, 1920, **53**, [*B*], 2162—2164).—The method described by Debye and Scherrer (A., 1917, ii, 437) for the examination of crystalline powders by means of *X*-rays has been applied to the examination of biological material, chiefly fibres. The material was crushed, pressed into a small capillary, and exposed to *X*-rays,

as described (*loc. cit.*). Cotton, ramie, and wood-fibre all gave interference figures indicating rhombic symmetry, $a:b:c=0{\cdot}6935:1:0{\cdot}4467$. When a bundle of fibres was examined by a combination of the Debye-Scherrer and von Laue methods, evidence was obtained that the particles of cellulose are regularly orientated in the direction of the length of the fibre, that is, the direction of growth. Woody cellulose and crushed jute gave results almost identical with the above, and it is consequently impossible to say whether the lignin is adsorbed by or combined with the cellulose. Viscose artificial silk appears to be crystalline, but the particles are not regularly orientated in the direction of the fibre. Acetylcellulose silk appears to be amorphous.

Rice-, maize-, and wheat-starch show rhombic symmetry, $a:b:c=0{\cdot}7252:1:0{\cdot}5509$, whilst glycogen is amorphous. Degummed silk shows a crystalline structure, but human hair is amorphous. E. H. R.

Certain Sulphur Derivatives of *iso*Propylamine. MARGARETHE BÖSE (*Ber.*, 1920, **53**, [*B*], 2000—2002).—2-Thiol-4-methylthiazoline, $\begin{matrix}\text{CHMe·N}\\ \text{CH}_2\text{—S}\end{matrix}\!\!>\!\text{C·SH}$ (Gabriel and Ohle, A., 1917, i, 564), is slowly hydrolysed by boiling 20% hydrochloric acid to carbon dioxide, hydrogen sulphide, and *α-thiol*iso*propylamine hydrochloride*, $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}SH,HCl$, needles, m. p. 94° after softening at 90°; the corresponding *picrate* crystallises in short prisms, m. p. 123°. An aqueous solution of the hydrochloride is oxidised by iodine to *ββ′-diaminodipropyl disulphide*,

$$(NH_2{\cdot}CHMe{\cdot}CH_2)_2S_2,$$

a powerfully alkaline oil, which gives a *hydrochloride*, small needles, m. p. 212° after previous darkening, and a *picrate*, rectangular plates, m. p. 201° (decomp.) after darkening at 198°; the *dibenzoyl* derivative crystallises in leaflets, m. p. about 170° after marked softening at 157°. The hydrochloride is transformed by boiling benzoyl chloride into 2-*phenyl*-4-*methylthiazoline*,

$$\begin{matrix}\text{CHMe·N}\\ \text{CH}_2\text{—S}\end{matrix}\!\!>\!\text{CPh},$$

colourless oil, which is identified in the form of its *picrate*, rhombic plates, m. p. 124° after softening at 119°, and *dichromate*, $(C_{10}H_{11}NS)_2H_2Cr_2O_7$, orange-coloured precipitate, which decomposes below 100°. H. W.

The Stereochemistry of the Ruthenium Atom. A. WERNER and AL. P. SMIRNOFF (*Helv. Chim. Acta*, 1920, **3**, 737—747). —The discovery of a series of salts of the structure

$$\left[\begin{matrix}\text{NO}\\ \text{HO}\end{matrix}\,\text{Ru(NH}_3)_4\right]X_2$$

(Werner, A., 1907, ii, 560) proved that the co-ordination number of ruthenium is 6, and now the conversion of this series into another with ethylenediamine instead of ammonia brings

ruthenium completely into line with the other metals of the platinum group as far as the co-ordination theory is concerned (compare A., 1920, i, 598).

Ruthenic chloride is converted into potassium pentachloronitrosorutheneate, and then into nitrosohydroxotetrammineruthenium bromide (Werner, *ibid.*; new details are given). The latter is warmed with 10% ethylenediamine solution, and, after most of the ammonia is expelled, the solution is cooled and mixed with potassium iodide. The crude iodide of the new series is precipitated, contaminated by colloidal ruthenium. To remove the latter, the salt is dissolved in water and partly precipitated by silver nitrate, when the filtrate is found to be free from the impurity, and can be "salted out" with potassium iodide again.

The following *nitrosohydroxodiethylenediamineruthenium* salts, $\left[\begin{smallmatrix}NO\\HO\end{smallmatrix} Ru\ en_2\right]X_2$, are described: *iodide*, golden-yellow leaflets; *bromide*, thin, yellow prisms; *chloride*, slender, yellow needles; *nitrate*, stout, dark yellow prisms; *sulphate*, yellow needles; *perchlorate*, large, flat, yellow prisms; d-*α-bromo-π-camphorsulphonate*, stout, yellow prisms; d-*camphor-α-sulphonate*, large, yellow leaflets. The salts of the optically active acids are inactive, and no resolution of the base has been effected, in addition, by *d*-camphoric acid, *d*-tartaric acid, or *d*-nitrocamphor. The nitroso- and hydroxyl groups are therefore probably in the *trans*-positions (1 : 6). J. C. W.

Preparation of Derivatives of Hexamethylenetetramine. J. D. Riedel (D.R.-P. 324203; from *Chem. Zentr.*, 1920, iv, 473).—Quaternary bases of hexamethylenetetramine are treated with cholic acid. The cholates of hexamethylenetetramine methyl hydroxide and hexamethylenetetramine ethyl hydroxide crystallise in prisms. They can be used therapeutically for gall-stones.

S. S. Z.

Calcium Cyanamide. Naoto Kameyama (*J. Coll. Eng., Tokyo Imp. Univ.*, 1920, **10**, 173—207, 209—247, 249—263).—To prepare calcium cyanamide in a pure state, the methods of igniting carbamide, cyanamide, or other amides of carbonic acid were investigated. If carbamide is employed, calcium cyanate is formed as an intermediate product at temperatures below 300°, but it is transformed into cyanamide slowly at 340—360°, and rapidly above 450°. Oxidation of the cyanamide is avoided by heating for a short time only—5 to 7 minutes at 800°. The product of the ignition consists of a mixture of cyanamide, calcium carbonate, and calcium oxide; with initial proportions of carbamide and lime of 1 : 2, 1 : 1½, and 1 : 1, the amounts of calcium cyanamide in the product are found to be 16·5, 24, and 34%. If the materials are ignited in a current of nitrogen, a quantitative yield results; in air, 92—98% of the theoretical yield is obtained. It is preferable to employ dicyanodiamide instead of carbamide, as the product contains a higher percentage of cyanamide. The most suitable temperature is 900—1000°, in order to decompose most of the

calcium carbonate formed, the time of ignition being about ten minutes. Cyanate is not formed as an intermediate product when dicyanodiamide is used. About 50—53% of cyanamide is found in the product after ignition, but 90% may be reached by further heating with excess of dicyanodiamide, and 99% if the ignition is carried out in a current of nitrogen. The action on cyanamide of oxygen, carbon dioxide, and carbon monoxide was investigated. Oxygen acts rapidly at 420—450°, with formation of calcium carbonate and nitrogen, but free carbon is not separated. Up to 1070°, carbon dioxide reacts, with formation of calcium oxide and nitrogen. Above 1110°, however, separation of carbon takes place, owing to the action of the carbon monoxide produced: $CaCN_2 + CO = CaO + 2C + N_2$. Carbon monoxide exerts no action on calcium cyanamide up to 1000° in absence of catalysts, but if carbon dioxide is produced from the monoxide, the cyanamide may become oxidised. Even in the absence of catalysts, as shown above, carbon monoxide reacts at temperatures above 1140°. The heat of combustion of calcium cyanamide, determined with the aid of sucrose, was found to be 155,020 cal. per gram-mol. at constant volume, and 154,730 cal. at constant pressure, and, from calculation, the heat of formation is $Ca + C$ diam. $+ N_2 = CaCN_2 + 91{,}480$ cal., or $Ca + C$ amorph. $+ N_2 = CaCN_2 + 94{,}820$ cal. W. J. W.

Complex Compounds of Thiocyanates and Arsenious Acid. FRITZ EPHRAIM (*Helv. Chim. Acta*, 1920, **3**, 800—805).—When arsenic trioxide, potassium hydroxide, and potassium thiocyanate are mixed in concentrated solutions, precipitates are obtained of products varying in composition between the limits $KCNS : As_2O_3$, 2 : 3 and 1 : 2, and $KOH : As_2O_3$, 0 : 1 and 1 : 1. These are mostly freely soluble in water, and crystallise well; for example, one approximating to $K_2O,3As_2O_3,2KCNS,4H_2O$, forms long, silky needles, but they decompose when crystallised from hot water into the *compound*, $KCNS,2As_2O_3$, which separates from the hot solution in indefinite, hexagonal, microscopic platelets. Using sodium salts, an asbestos-like mass approximating to

$$2NaOH,NaCNS,2As_2O_3,4H_2O$$

has also been prepared. J. C. W.

The Possible Asymmetry of the Aliphatic Diazo-compounds. C. S. MARVEL and W. A. NOYES (*J. Amer. Chem. Soc.*, 1920, **42**, 2259—2278).—Unsuccessful attempts were made to prepare optically active diazo-compounds from active amino-esters, using the method of Curtius (A., 1885, 883). Ethyl *dl*-phenylaminoacetate gave an *acetyl* derivative, m. p. 65—66°, and a *carbethoxy*-derivative, m. p. 57°. Impure *ethyl phenyldiazoacetate* was obtained by the action of sodium nitrite and acetic acid on ethyl phenylaminoacetate hydrochloride in sodium acetate solution. All attempts to purify this diazo-ester led to its decomposition, giving ethyl mandelate. Attempts to prepare the optically active diazo-ester from ethyl *l*-phenylaminoacetate hydro-

chloride were not successful, but this *l*-ester gave an *acetyl* derivative, m. p. 69—70°.

*Ethyl α-diazo-*n*-hexoate*, b. p. 75—78°/10 mm., n_D^{26} 1·453, was readily obtained from the corresponding amino-ester hydrochloride. When decomposed by dilute acids, the diazo-ester gave ethyl α-hydroxy-*n*-hexoate and ethyl Δ^{α}-hexenoate. *Ethyl* l-*α-amino-*n*-hexoate*, b. p. 86—87°/12 mm., and its *hydrochloride*, $[\alpha]_D$ −7·25°, were prepared from the *l*-amino-acid, and *ethyl* d-*α-amino-*n*-hexoate*, b. p. 85°/10 mm., and its *hydrochloride* were prepared from the *d*-amino-acid. The diazo-esters prepared from these optically active esters were, however, inactive, and when decomposed by dilute acids they gave optically inactive products.

α-Bromohexoic acid when heated with thionyl chloride yielded *α-bromo-*n*-hexoyl chloride*, b. p. 102—105°/30 mm., which condensed with glycine in the presence of sodium hydroxide to give *α-bromo-*n*-hexoylglycine*, m. p. 114—115°, from which, by the action of ammonium hydroxide, *α-amino-*n*-hexoylglycine*, m. p. 226°, was readily obtained. This dipeptide readily gave an *ethyl ester hydrochloride*, which, when acted on by sodium nitrite and acetic acid, gave the *ethyl* ester of *α-hydroxy-*n*-hexoylglycine*, m. p. 90—91°.

Ethyl α-amino-octoate, b. p. 110°/10 mm., n_D^{21} 1·436, gave a *hydrochloride*, m. p. 76—77°, which, when diazotised, gave an impure diazo-ester readily decomposing into *ethyl α-hydroxy-octoate*, b. p. 80—85°/7 mm.

A second unsuccessful attempt to prepare pure diazo-compounds consisted in an application of the method of Oppe (compare A., 1913, i, 534). Methylphthalimidine was readily converted into its *nitroso*-derivative, m. p. 86·5—87°, but the latter could not be converted into *o*-carbethoxyphenylmethyldiazomethane. As it was not found possible to resolve methylphthalimidine, this work was abandoned. Similarly, attempts to prepare a nitroso-derivative from *sec.*-butylurethane were not successful.

Under certain conditions, the treatment of optically active amino-ester hydrochlorides with nitrous acid gave optically active hydroxy-esters, and it is suggested that if the diazo-ester is an intermediate compound, this is evidence for the existence of an asymmetric diazo-compound. W. G.

Constitution of Acetatomercuriformic Esters. WALTER SCHOELLER (*Ber.*, 1920, **53**, [*B*], 2144—2147).—Methyl acetatomercuriformate has been formulated $CH_3 \cdot CO \cdot O \cdot Hg \cdot CO_2Me$ by Schoeller, Schrauth, and Essers (A., 1913, i, 1162; 1920, i, 225), but has more recently been considered by Manchot (A., 1920, i, 520) to be a simple additive compound, chiefly on account of its susceptibility to halogen acids, but not to oxy-acids, and its behaviour towards alkyl iodides. The former property, however, only represents an extreme case of the general behaviour of mercurated compounds towards halogen acids, and has an exact parallel in their behaviour towards ammonium sulphide, whilst the latter reaction

is regarded as insufficient evidence of additive structure. The constitutive nature of the substance is established by its reduction with activated aluminium to methyl formate, and by its hydrolysis with aqueous sodium hydroxide, in accordance with the scheme: $CH_3 \cdot CO \cdot O \cdot Hg \cdot CO_2R + 2NaOH = CH_3 \cdot CO_2Na + HO \cdot R +$
$HO \cdot Hg \cdot CO_2Na \longrightarrow Hg + HO \cdot CO_2Na$, and also by the quantitative formation of methyl chloroformate from methyl chloromercuriformate when acted on by iodine.

The results of the investigation of the mercuration of cinnamic esters (A., 1911, i, 595) are in good agreement with Biilmann's observations in the same field (A., 1910, i, 346), and are readily interpreted on the hypothesis of structural compounds. Confirmation of this has been obtained by the isolation of substances containing an asymmetric carbon atom by the simultaneous addition of the mercuri-complex and the alkyloxy-group at the double bond; the substances are to be described shortly. H. W.

Decomposition of Hydrogen Peroxide by Organic Compounds and its Bearing on the Catalase Reaction. SERGIUS MORGULIS and V. E. LEVINE (*Science*, 1920, **52**, 202—204).—A group of aromatic hydrocarbons and their derivatives give the typical catalase reaction. Benzene reacts most vigorously, 0·2 c.c. liberating 20 c.c. of oxygen from hydrogen peroxide in a manner exactly resembling the effect of an active enzyme preparation. The aromatic hydrocarbons of the benzene group form a series of gradually decreasing power to liberate oxygen from hydrogen peroxide according to the number of methyl groups attached to the ring, thus, benzene>toluene>xylene>mesitylene. The reaction is not general for the aromatic hydrocarbons, but is specific for the benzene series. Hydrocarbons with more than one ring and heterocyclic compounds give negative results. The attachment of a carboxyl, hydrazino-, or hydroxyl group to the ring renders the compound incapable of decomposing hydrogen peroxide, whilst a nitro-, amino-, or aldehydo-group, or a halogen atom, lessens, but does not destroy, the action. Adrenaline and its hydrochloride decompose hydrogen peroxide feebly. The decomposition is not caused by changes in surface tension. CHEMICAL ABSTRACTS.

Ethylenic Isomerism of the Styrenes Monobrominated in the Side-chain. CHARLES DUFRAISSE (*Compt. rend.*, 1920, **171**, 960—963).—Two isomeric monobromostyrenes are known, and the author has now prepared the third. One of the isomerides (*A*), m. p. 6—7°, b. p. 107°/22—23 mm., D^{20} 1·422, $n_D^{20.5}$ 1·6094, is obtained by heating sodium dibromo-β-phenylpropionate in aqueous solution with sodium carbonate. The second isomeride (*B*), m. p. $-43°$, b. p. 71°/7—8 mm., D^{20} 1·406, $n_D^{19.5}$ 1·5881, is prepared by the action of dry hydrogen bromide on an acetic acid solution of phenylacetylene. The third *isomeride* (*C*), m. p. $-8°$ to $-7°$, b. p. 71°/6—7 mm., D^{20} 1·426, $n_D^{22.5}$ 1·5990, is obtained by heating phenylbromostyrylketen with powdered sodium hydroxide. When the two isomerides, *A* and *C*, are brominated, they

both give $\alpha\beta\beta$-tribromoethylbenzene, and consequently they are stereoisomerides having the constitution CHPh:CHBr. The isomeride *B*, on bromination, gives $\alpha\alpha\beta$-tribromoethylbenzene, and therefore has the constitution CPhBr:CH_2. W. G.

Formation of 2 : 3 : 6-Trinitrotoluene in the Nitration of Toluene. ROYSTON BARRY DREW (T., 1920, **117**, 1615—1618).

Products of Detonation of Trinitrotoluene. C. E. MUNROE and S. P. HOWELL (*Proc. Amer. Phil. Soc.*, 1920, **59**, 194—223).—For the analysis of the products of detonation of trinitrotoluene, the material selected had a f. p. 80·2° and a nitrogen content of 18·32%, as determined by Dumas' method, and 18·14% as found by Orndorff's modification of the Kjeldahl method, in which red phosphorus and hydrogen iodide, with or without iodine, are employed as reducing agent, and copper sulphate, sodium sulphate, and sulphuric acid as digestion agent. The tests were carried out in a Bichel pressure gauge, the charges being wrapped in tin-foil and fired with a No. 8 detonator, and the gaseous products were analysed in the Burrell modification of the Orsat apparatus (A., 1916, ii, 260). In calculating the results, corrections were applied for nitrogen in the detonator and in the residual air, and as a check on the accuracy of the observations, a comparison was made with the original total nitrogen content. From ten experiments with charges increasing by 50 grams from 25 grams to 450 grams, with loading densities of from 0·0016 to 0·003, the maximum and minimum percentages of the gases found were as follows: CO_2, 6·4, 1·1; CO, 60·7, 53·2; H, 27·6, 19·9; CH_4, 2·3, 0·1; N, 15·6, 13·3. In every case an odour of ammonia was distinguishable; its amount in a single case was found to be 0·034%. Two experiments with trinitrotoluene charges of density 0·86 and 1·50 respectively, indicated no difference in the gas analysis, nor was any alteration produced by using different detonating agents, such as tetryl in one case and fulminate–chlorate composition in another. After each experiment, some solid combustion products were found in the gauge; three 200-gram charges gave 5·5, 8·0, and 9·25%, and a 400-gram charge gave 3·75%. The amount of solid matter appears to diminish with the weight of the charge and to increase with its density. The composition of the deposit was found to be: moisture, 0·25%; ash, 77·10%; H, 0·33%; C, 34·34%; N, 1·01%; S, 3·97%; eliminating contaminating substances from the gauge, detonator, and wrapper, this gives H, 1·03%; C, 96·07%; N, 2·90%. The amount of the gases absorbed by the solid combustion products was found to be 6·11 c.c. per gram, the composition being CO_2, 71·3%; CH_4, 1·0%; N, 27·7%. The quantity is not sufficient to affect the analysis of the gaseous products. W. J. W.

The Crystal Forms of some Substituted Amides of Toluene-*p*-sulphonic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 347—362).—The crystals of a

number of N-substituted derivatives of toluene-*p*-sulphonamide and nitrotoluene-*p*-sulphonamide, prepared by Van Romburgh (A., 1902, i, 607), are described. (The orientation of the nitro-group in the derivatives of the latter substance is not stated, but it appears probable that *o*-nitrotoluene-*p*-sulphonamide is intended.)

Nitrotoluene-*p*-sulphonamide, m. p. 141°, large, transparent crystals from ethyl acetate, monoclinic, pseudo-rhombic, $a:b:c = 1\cdot2289:1:1\cdot1812$, $\beta = 90°$, $D^{15°}$ 1·612.

Toluene-*p*-sulphonmethylamide, m. p. 76°, small, colourless, rectangular plates from alcohol, rhombic bipyramidal, $a:b:c = 1\cdot0358:1:2\cdot6074$, $D_4^{15°}$ 1·340.

Nitrotoluene-*p*-sulphonmethylamide, m. p. 91°, pale yellow prisms from ethyl acetate, monoclinic prismatic, $a:b:c = 1\cdot0522:1:0\cdot3948$, $\beta = 86°40\frac{1}{2}'$, $D^{16°}$ 1·485.

Toluene-*p*-sulphonmethylnitroamide, m. p. 60°, almost colourless, stout, short prisms or flat needles from a mixture of light petroleum and ether, monoclinic prismatic, $a:b:c = 1\cdot3210:1:0\cdot6892$, $\beta = 78°6'$, D 1·454.

Toluene-*p*-sulphonethylamide, m. p. 64°, colourless, thin plates or prisms from a mixture of alcohol and ether, triclinic pedial, $a:b:c = 0\cdot6481:1:0\cdot4136$, $\alpha = 77°39\frac{1}{2}'$, $\beta = 88°6'$, $\gamma = 102°55\frac{1}{2}'$, D 1·307.

Toluene-*p*-sulphondiethylamide, m. p. 59°, thin, colourless, six-sided plates or tables from a mixture of alcohol and ethyl acetate, monoclinic prismatic, $a : b : c = 1\cdot0149:1:0\cdot6762$, $\beta = 72°1'$, $D^{15°}$ 1·230.

Toluene-*p*-sulphonethylnitroamide, m. p. 69°, large, colourless, six-sided tables from ether, monoclinic prismatic, $a:b:c = 1\cdot0178:1:1\cdot1005$, $\beta = 88°11'$, D 1·450.

Nitrotoluene-*p*-sulphonethylnitroamide, m. p. 76°, thin, yellow, lustrous plates from hot carbon tetrachloride solution, monoclinic, probably sphenoidal, $a:b:c = 0\cdot4812:1:0\cdot8766$, $\beta = 85°5'$, D 1·555.

Toluene-*p*-sulphonbenzylamide, large, colourless crystals from a mixture of ether and alcohol, triclinic pinacoidal, $a:b:c = 0\cdot9778:1:0\cdot8991$, $\alpha = 83°24\frac{1}{2}'$, $\beta = 91°33'$, $\gamma = 95°26'$, $D^{17°}$ 1·313.

Nitrotoluene-*p*-sulphonbenzylnitroamide, m. p. 153°, small, lustrous crystals from ethyl acetate, triclinic pinacoidal, $a:b:c = 1\cdot8095:1:1\cdot3139$, $\alpha = 100°50'$, $\beta = 104°43'$, $\gamma = 65°33'$, $D^{17°}$ 1·530.

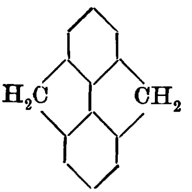
Toluene-*p*-sulphonpiperidide, m. p. 98°, colourless, lustrous, rectangular crystals from ether, rhombic bipyramidal, $a:b:c = 0\cdot7474:1:0\cdot3790$, $D^{15°}$ 1·281.

Nitrotoluene-*p*-sulphonpiperidide, m. p. 108°, large, yellow, lustrous crystals from ethyl acetate, monoclinic prismatic, $a:b:c = 0\cdot7466:1:1\cdot5713$, $\beta = 78°39'$, $D^{15°}$ 1·384. E. H. R.

The Sensitiveness of Hexanitrodiphenyl to Mechanical Influences compared with that of Hexanitro-compounds of similar Constitution. C. F. VAN DUIN (*Rec. trav. chim.*, 1920, **39**, 685—688).—Using the method previously described (A.,

1920, i, 307), it is shown that hexanitrodiphenyl is more sensitive to mechanical shock than trinitrobenzene, but is much less sensitive than trinitrophenylmethylnitroamine or than hexanitrodiphenyl oxide or sulphide. W. G.

Attempted Synthesis of a Hydrocarbon, $C_{14}H_{10}$. RICHARD MEYER, WILHELM MEYER, and KURT TAEGER (*Ber.*, 1920, **53**, [*B*], 2034—2052).—Further attempts to prepare a hydrocarbon of the annexed formula are described (compare Meyer and Wesche, A., 1917, i, 340, 341) which, up to the present, have not led to the desired result.



Diphenyl condenses with an excess of formaldehyde or methylal in the presence of glacial acetic or concentrated sulphuric acid, yielding bisdiphenylylmethane, $CH_2(C_6H_4{\cdot}C_6H_5)_2$, leaflets, m. p. 159°.

Diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid (Mayer, A., 1911, i, 869) is converted into fluorenone, m. p. 84—85°, by distillation with lime, and is not changed by fuming hydrochloric acid at 150°, 180°, or 200°

2 : 6 : 2′ : 6′-Tetrabromodiphenyl is prepared by the following series of reactions: *p*-nitroaniline is converted by bromine in methyl-alcoholic solution into 2 : 6-dibromo-*p*-nitroaniline, m. p. 202°, which is transformed into 3 : 5-dibromonitrobenzene, long, almost colourless needles, m. p. 106°, by ethyl nitrite (*m*-bromonitrobenzene, m. p. 55—56°, is formed as by-product), or, preferably, by the addition of solid sodium nitrite to a boiling suspension of the base in a mixture of alcohol and concentrated sulphuric acid. The bromonitro-compound is converted by sodium hydroxide into 3 : 5 : 3′ : 5′-*tetrabromoazoxybenzene*, yellow leaflets, m. p. 196—197°, which is reduced by zinc dust and alkali to 3 : 5 : 3′ : 5′-*tetrabromoazobenzene*, golden-yellow needles, m. p. 244°, and by zinc dust and acetic acid in the presence of alcohol to 3 : 5 : 3′ : 5′-*tetrabromohydrazobenzene*, almost colourless needles, m. p. 182—183° (*monoacetate*, colourless needles; m. p. 204°; the diacetate cannot be prepared with acetic anhydride). The conversion of the hydrazo-compound into the benzidine derivative could only be accomplished with difficulty; dilute acids are without action, whilst concentrated hydrochloric acid gives mainly 3 : 5 : 3′ : 5′-tetrabromoazobenzene and 3 : 5-dibromoaniline. The best results were obtained by the use of a mixture of concentrated sulphuric acid (2 volumes) and water (1 volume) at 100°. 2 : 6 : 2′ : 6′-*Tetrabromobenzidine* forms colourless needles, m. p. 180°, and is a somewhat weak base, the salts of which are extensively hydrolysed by water. The *hydrochloride*,

$$C_{12}H_8N_2Br_4,2HCl,EtOH,$$

separates from absolute alcohol in colourless needles; the *diacetate* forms small crystals, m. p. 269—270° (decomp.). [In contrast with 3 : 5 : 3′ : 5′-tetrabromobenzidine (Mills, T., 1894, **65**, 55), the

present base does not appear to yield a tetra-acetate.] 2:6:2′:4′-*Tetrabromo*-4:6′-*diaminodiphenyl*, colourless needles, m. p. 242°, is obtained as by-product in the benzidine transformation; it yields a *dihydrochloride*, colourless, crystalline powder, and a *diacetate*, coarse, rhombic prisms, m. p. 331°. Diazotisation of 2:6:2′:6′-tetrabromobenzidine, and subsequent treatment of the diazo-solution with boiling alcohol, leads to the isolation of small amounts of 2:6:2′:6′-*tetrabromodiphenyl*, large, octahedral crystals, m. p. 215°, together with larger quantities of an amorphous, red powder, which decomposes without melting above 320°, and appears to have the composition $C_{24}H_{13}N_5Br_8$. Attempts to obtain the desired hydrocarbon or its derivatives from 2:6:2′:6′-tetrabromodiphenyl by the use of methylene bromide and sodium or ethyl disodiomalonate were uniformly unsuccessful, the material being recovered unchanged in spite of considerable variation in the experimental conditions; in one case, with ether as solvent, small quantities of diphenyl were produced. Tetrabromodiphenyl and methylene bromide did not react in the presence of copper powder.

Unsuccessful attempts to prepare 2:6:2′:6′-tetrabromodiphenyl-4:4′-dicarboxylic acid by the bromination of diphenyl-4:4′-dicarboxylic acid are also described. H. W.

Naphthalenesulphonic Acids. I. Sparingly Soluble Salts of certain Naphthalenesulphonic Acids. JOSEPH A. AMBLER (*J. Ind. Eng. Chem.*, 1920, **12**, 1081—1085).—The α- and β-naphthylamine salts of different naphthalenesulphonic acids were prepared by mixing solutions of molecularly equivalent quantities of the acid or its sodium or potassium salt and the hydrochloride of the organic base, washing the crystallised salts with cold water, and drying them at 100° in a vacuum oven. All are sparingly soluble in water, the salt of the 1:5-disulphonic acid being the most insoluble, and all are hydrolysed by boiling water.

α-*Naphthylamine naphthalene*-1-*sulphonate*,

$$C_{10}H_7{\cdot}NH_2,C_{10}H_7{\cdot}SO_3H,$$

forms glistening crystals made up of overlapping plates, n_D $\alpha=1{\cdot}552$, which is its most distinctive characteristic. It melts and decomposes at 232°. β-*Naphthylamine naphthalene*-1-*sulphonate* crystallises in large, glistening, diamond-shaped plates, whilst if the hot solution is too concentrated, it first forms a stiff jelly. It blackens at 202° and melts at 211°, n_D $\alpha=1{\cdot}620$, $\beta=1{\cdot}670$. α-*Naphthylamine naphthalene*-2-*sulphonate* melts and decomposes at 240—242°, and has n_D $\alpha=1{\cdot}600$, $\beta=1{\cdot}650$, and $\gamma=1{\cdot}725$. β-*Naphthylamine naphthalene*-2-*sulphonate* crystallises in insoluble, microscopic plates, m. p. 276—279° (decomp.). It has n_D $\alpha=1{\cdot}640$, $\gamma=1{\cdot}730$. *Ferrous naphthalene*-2-*sulphonate*, $Fe(C_{10}H_7SO_3)_2,6H_2O$, separates in large, colourless, glistening plates when ferrous chloride is added to a cold solution of naphthalene-β-sulphonic acid or its salts. It dissolves sparingly in cold, but readily in hot, water. It loses its water of crystallisation at 150—160°. It gives n_D $\alpha=1{\cdot}500$ and $\gamma=1{\cdot}660$, the

unusually low value of α being a distinctive characteristic. *α-Naphthylamine naphthalene-*1 : 5*-disulphonate*,

$$(C_{10}H_7\cdot NH_2)_2,C_{10}H_6(SO_3H)_2,$$

forms a heavy, granular precipitate, which is almost insoluble in boiling water. It is sparingly soluble in a mixture of 4 vols. of alcohol and water, n_D $\alpha=1\cdot600$, $\gamma=1\cdot795$. *β-Naphthylamine naphthalene-*1 : 5*-disulphonate* crystallises in small plates not melting below 280°, and having n_D $\alpha=1\cdot631$, $\beta=1\cdot647$, and $\gamma=1\cdot755$. An acid salt is formed having $\alpha=1\cdot550$. *α-Naphthylamine naphthalene-*1 : 6*-disulphonate* decomposes at 265—267°. It crystallises in rods, showing n_D $\alpha=1\cdot583$, $\beta=1\cdot730$, $\gamma=1\cdot770$. *β-Naphthylamine naphthalene-*1 : 6*-disulphonate* forms flat, lustrous needles soluble in hot water, and having n_D $\alpha=1\cdot550$. *α-Naphthylamine naphthalene-*2 : 6*-disulphonate* crystallises in minute needles not melting below 280°. It has n_D $\alpha=1\cdot583$, $\beta=1\cdot640$, and $\gamma=1\cdot690$. *β-Naphthylamine naphthalene-*2 : 6*-disulphonate* crystallises in microscopic plates and needles, with n_D $\alpha=1\cdot610$, $\beta=1\cdot634$, and $\gamma=1\cdot830$. *α-Naphthylamine naphthalene-*2 : 7*-disulphonate* crystallises in needles, decomposing, without melting, above 220°, and having n_D $\alpha=1\cdot560$, $\beta=1\cdot650$, and $\gamma=1\cdot675$. *β-Naphthylamine naphthalene-*2 : 7*-disulphonate* crystallises in needles not melting below 280°, with n_D $\alpha=1\cdot530$, $\beta=1\cdot700$, and $\gamma=1\cdot740$.

C. A. M.

Action of Furfuraldehyde on Primary Aniline Bases and Aromatic Amino-acids. OTTO FISCHER, A. BALLING, and R. ALDINGER (*J. pr. Chem.*, 1919, [ii], **100**, 105—114).—The dyes formed by the action of aniline and its salts on furfuraldehyde (Stenhouse), as a result of the opening of the furan ring (Zincke and Mühlhauser, A., 1906, i, 33; Dieckmann and Beck, *ibid.*, 109; König, *ibid.*, 109), have hitherto been known only in the form of their salts. In certain cases, however, the free bases have now been obtained. Thus, from *o*-nitroaniline, the *di-o-nitroanilide* of *hydroxyglutaconaldehyde*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CH{:}CH\cdot CH{:}C(OH)\cdot CH{:}N\cdot C_6H_4\cdot NO_2,$$

brown pyramids or leaflets, m. p. 149°, is produced. Similarly constituted *compounds* are furnished by *m*-nitro-*p*-toluidine ($C_{19}H_{18}O_5N_4$, red prisms, decomp. about 175°; hydrochloride,

$$C_{19}H_{18}O_5N_4,HCl+H_2O\ (?),$$

a violet powder); *m*-nitroaniline ($C_{17}H_{14}O_5N_4$, orange needles, m. p. 212—215°, decomp.); *o*-aminobenzoic acid ($C_{19}H_{16}O_5N_2$, yellow crystals, m. p. *ca.* 180°); *p*-aminobenzoic acid ($C_{19}H_{16}O_5N_2$, a brown, crystalline powder, m. p. *ca.* 227°, decomp.). Normal *furylidene* derivatives are obtained from *p*-nitroaniline ($C_{11}H_8O_3N_2$, yellow needles, m. p. 139—140°), *m*-nitro-*o*-toluidine ($C_{12}H_{10}O_3N_2$, yellow needles, m. p. 130°), *p*-nitro-*o*-toluidine ($C_{12}H_{10}O_3N_2$, yellow prisms, m. p. 75°), 6-nitro-*m*-4-xylidine ($C_{13}H_{12}O_3N_2$, yellow, transparent leaflets, m. p. 124°), *p*-aminodimethylaniline ($C_{13}H_{14}ON_2$, yellow prisms, m. p. 100—101°), *o*-chloroaniline ($C_{11}H_8ONCl$, yellow prisms, m. p. 66—67°), and *p*-chloroaniline ($C_{11}H_8ONCl$, red prisms, m. p. 48—50°).

J. K.

Crystalline Acetylphenylurethane. D. R. NIJK (*Rec. trav. chim.*, 1920, **39**, 699—703).—Acetylphenylurethane,

$NPhAc\cdot CO_2Et$,

can be obtained in a crystalline form either by the action of ethyl chloroformate on sodium acetanilide in dry benzene or by the acetylation of phenylurethane with acetic anhydride and acetyl chloride. It crystallises in rhombic, bipyramidal crystals, $a:b:c=1\cdot2323:1:1\cdot5141$, m. p. 59°. *p*-Acetylphenylurethane,

$C_6H_4Ac\cdot NH\cdot CO_2Et$,

has m. p. 158°. W. G.

The Dihydronaphthalene Series. I. The *ar*-Dihydro-α-naphthylamines and their Derivatives. FREDERICK MAURICE ROWE and ESTHER LEVIN (T., 1920, **117**, 1574—1579).

The Condensation of Formaldehyde with *o*-Nitrophenol. JACOB B. FISHMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 2288—2297).—In the condensation of formaldehyde with *o*-nitrophenol in the presence of hydrochloric acid, the yield of 3-nitro-4-hydroxybenzyl alcohol and of 3-nitro-2-hydroxybenzyl alcohol is controlled by the concentration of the acid, the molecular proportion of formaldehyde, and the duration of heating. The best yield of 3-nitro-4-hydroxybenzyl alcohol is obtained by heating 60 grams of formaldehyde solution (40%) with 100 grams of *o*-nitrophenol and 500 grams of concentrated hydrochloric acid for six hours. The second alcohol, 3-*nitro*-2-*hydroxybenzyl alcohol*, m. p. 75°, may be separated from its isomeride, owing to the fact that its *potassium* salt is insoluble in alcohol. Further, the 2-hydroxy-alcohol dissolves readily in concentrated sulphuric acid, whilst its isomeride is only sparingly soluble. On oxidation, 3-nitro-2-hydroxybenzyl alcohol gives 3-nitrosalicylic acid, m. p. 144°. On methylation, it gives 3-*nitro*-2-*methoxybenzyl alcohol*, m. p. 42°, which, on oxidation, gives 3-*nitro*-2-*methoxybenzoic acid*, m. p. 191—192°. W. G.

Some Derivatives of 3-Nitro-4-hydroxybenzyl Alcohol. JACOB B. FISHMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 2297—2302. Compare preceding abstract).—By controlled oxidation with potassium permanganate, 3-nitro-4-hydroxybenzyl alcohol gives, in turn, 3-nitro-4-hydroxybenzaldehyde, m. p. 142°, and 3-nitro-4-hydroxybenzoic acid, m. p. 183—184°, thus furnishing a new method of preparing "Orthoform-New" (methyl 3-amino-4-hydroxybenzoate).

Attempts to reduce 3-nitro-4-hydroxybenzyl alcohol were not successful, but its methyl and ethyl ethers were readily reduced. 3-Nitro-4-methoxybenzyl alcohol, when reduced with ferrous sulphate in ammoniacal solution, gave 3-*amino*-4-*methoxybenzyl alcohol*, m. p. 95°, which, on diazotisation, gave 2-*methoxy*-5-*hydroxymethylbenzenediazonium chloride*, yielding, when submitted to the Sandmeyer reaction with copper cyanide, 3-*cyano*-4-*methoxybenzyl alcohol*, m. p. 81°. Similarly, 3-*nitro*-4-*ethoxy*-

benzyl alcohol, m. p. 66°, gave, in turn, *3-amino-4-ethoxybenzyl alcohol*, m. p. 83°, and *2-ethoxy-5-hydroxymethylbenzenediazonium chloride*. Both these diazonium chlorides are stable compounds, and can be digested in aqueous solutions for hours without change.

W. G.

The Contact Decomposition of Cholesterol. The Theory of Petroleum Formation. WILHELM STEINKOPF [with HANS WINTERNITZ, WILHELM ROEDERER, and AARON WOLYNSKI] (*J. pr. Chem.*, 1919, [ii], **100**, 65—85).—The suggestion that the optically active constituents of petroleum originate from cholesterol and its derivatives (Engler and Hullard, *Zeitsch. angew. Chem.*, 1908, **21**, 1585) readily accounts for most of the facts, with the exception that whilst the decomposition products hitherto obtained from cholesterol are all dextrorotatory, certain fractions of petroleum have been found to be slightly lævorotatory (Engler, "Neuere Ansichten über die Entstehung des Erdöls," 1907, 61). Curves are now presented, however, which show that the lævorotation of cholesterol, heated alone at 150° or 200°, or in presence of kieselguhr at 150°, suffers a gradual diminution to a minimum value, but not owing to racemisation, since an increase subsequently occurs; in presence of quartz at 200°, the rotation was continually diminished, and ultimately converted into a dextrorotation. At 280—300°, equal parts of cholesterol and kieselguhr, when rapidly heated, gave a cholesterylene, m. p. 71°, $[\alpha]_D$ −47°, in all probability identical with the product described by Mauthner and Suida (A., 1904, i, 49), since, by absorption of four atomic proportions of hydrogen, it was converted into a cholestan, m. p. 71°, $[\alpha]_D$ +25·46°, which corresponds closely with ψ-cholestane (Mauthner, A., 1909, i, 714). A similar mixture, when heated in a "pressure distillation tube" at 280°, furnishes one molecular proportion of water and an oil, of which almost half consisted of a cholesterylene, which is obtained more rapidly and in better yield by heating the mixture at 280—300° for seven to eight hours under ordinary pressure, and finally at 350° under 12 mm. It is thus obtained as a viscous, yellow oil with a blue fluorescence, b. p. 257—267°/12 mm., $[\alpha]_D$ +49·12°, D 0·9572, very probably identical with the product isolated by Mauthner and Suida from cholesteryl chloride (*loc. cit.*), since the physical properties of the latter were found to be in close agreement with those quoted. An oil similar in all respects, except that its fluorescence was green, was obtained by heating the solid cholesterylene with kieselguhr, and it therefore appears that, under the conditions prevalent in nature, cholesterol furnishes, first, a lævo-, and ultimately a dextro-rotatory, cholesterylene, these products subsequently giving products, some poorer, some richer, in hydrogen. Probably, as a result of changes of the latter kind, the optically active component of petroleum is generated, since liquid cholesterylene can be reduced in presence of palladium to a saturated, dextrorotatory, highly viscous product, which exhibits no fluorescence, and very closely resembles the

natural product separated by Halmai (*Diss.*, Karlsruhe, 1909). Traces of cholesteryl ether were produced when the mixture of cholesterol and kieselguhr was heated at 30° for a short time.

J. K.

The Action of Alcoholic Sodium Acetate Solution on Cholesterol Dibromide. I. Lifschütz (*Zeitsch. physiol. Chem.*, 1920, **111**, 253—256).—Polemical. A reply to Windaus and Lüders (A., 1920, i, 675).

S. S. Z.

Extraction of Sulphite Liquors with Ether and Benzene. Bror Holmberg (*Svensk Kemisk Tidskrift*, 1920, **32**, 56—67).—By shaking sulphite liquors with ether, a lactone has been isolated, m. p. 250—255° (according to the rate of heating), darkening at 240°, [α] −54° in acetone, which reduces ammoniacal silver oxide, but not Fehling's solution. It does not react with phenylhydrazine or semicarbazide, but forms a diacetyl derivative, $C_{24}H_{24}O_8$, m. p. 221—222°, $[\alpha]_D$ +73·5°, from which the lactone is regenerated by *N*-potassium hydroxide, and couples readily with diazotised benzidine. To the lactone, which can be converted into a hydroxy-acid, $C_{20}H_{22}O_7$, m. p. 172—173°, $[\alpha]_D$ +75°, and an amide of this acid, m. p. 139—140°, $[\alpha]_D$ +88°, is given the formula

$$\begin{array}{l}\mathrm{CHR\cdot CH\cdot CH_2} \\ \mathrm{CHR\cdot CH—CO}\end{array}\!\!>\mathrm{O} \quad \text{or} \quad \overbrace{\mathrm{CH_2\cdot CH}\!<\!\begin{array}{l}\mathrm{CHR}\\ \mathrm{CHR}\end{array}\!\!>\!\mathrm{CH\cdot CO}}^{\mathrm{O}},$$

where R is the guaiacol residue, $OMe\cdot C_6H_3\cdot OH$.

Chemical Abstracts.

Thionbenzoyl Chloride. H. Staudinger and Joseph Siegwart (*Helv. Chim. Acta*, 1920, **3**, 824—833).—With the exception of thiocarbonyl chloride, no member of the class R·CSCl appears to be known. The unusual results obtained in attempts to produce such compounds, and their possible use in the formation of thioketens, have caused the authors to direct special attention to the preparation of thionbenzoyl chloride. This has been achieved by the action of thionyl chloride on dithiobenzoic acid (Houben, A., 1906, i, 847). The reagents are mixed in concentrated ethereal solution, the thionyl chloride being in excess, kept for some hours at 100° in an atmosphere of carbon dioxide, and finally heated gradually in a high vacuum at 50° and 150—240°. The reaction is complex, and appears to involve many intermediate compounds, the production of free sulphur (or S_2O ?), and reactions between sulphur and thionyl chloride on the one hand and thionbenzoyl chloride and sulphur chloride on the other. The complex products decompose during the treatment in a high vacuum, and the chief distillates are thionbenzoyl chloride and sulphur chloride, the latter being condensed in a second receiver cooled to −80°. After repeated distillations at as low a temperature as possible, *thion-*

benzoyl chloride, $C_6H_5{\cdot}CSCl$, is obtained as a deep reddish-violet, mobile, evil-smelling liquid, b. p. 60—65°/0·2 mm. One of the intermediate products has been isolated during some experiments in the cold; it is probably *thionbenzoyl trisulphide*, $(C_6H_5{\cdot}CS)_2S_3$, and is a violet, crystalline powder, which yields thionbenzoyl chloride when heated with thionyl chloride. A by-product, obtained by the action of sulphur chloride on thiobenzoyl chloride, is a crystalline *compound*, m. p. 101—102°, probably represented by

$$(ClS{\cdot}CPhCl)_2S_2,$$

which is separated into its components by distillation in a high vacuum.

Thionbenzoyl chloride behaves otherwise as a true acid chloride. With aniline, it forms thionbenzanilide; with methyl alcohol it yields methyl thionbenzoate, $C_6H_5{\cdot}CS{\cdot}OMe$, a lemon-yellow oil, b. p. 114—114·5°/13 mm. (compare Matsui, A., 1909, i, 463); and with methyl mercaptan it gives *methyl dithiobenzoate*,

$$C_6H_5{\cdot}CS_2Me,$$

a bright red oil, b. p. 120°/13 mm. Methyl thiolbenzoate,

$$C_6H_5{\cdot}CO{\cdot}SMe,$$

b. p. 210—212°, is best obtained by shaking a cold, alkaline solution of the mercaptan with benzoyl chloride.

When thionbenzoyl chloride is heated at 100—120° in a current of oxygen, it is quickly changed into monoclinic sulphur and benzoyl chloride. J. C. W.

New Process of Manufacture of β-Dialkylaminoethylaminobenzoic Alkyl Esters. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 153827; addition to 128554).—β-Dialkylaminoethyl-*p*-aminobenzoic acid alkyl esters of the general formula $R_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2R'$ are obtained from β-chloroethyldialkylamines and *p*-aminobenzoic acid esters by heating the two compounds together in equimolecular proportions either with or without the use of a neutral diluent. For example, *ethyl β-diethylaminoethyl-*p*-aminobenzoate monohydrochloride* is prepared by adding 1 mol. of diethyl-β-chloroethylamine to a boiling solution of ethyl *p*-aminobenzoate in three times its weight of toluene, ebullition being then continued for one to two hours. On cooling the reaction mixture, crystals of the hydrochloride are deposited, which, when recrystallised from alcohol, melt at 156°. The following compounds obtained by the interaction of diethyl-β-chloroethylamine with the methyl, propyl, *N*-butyl, *iso*butyl, and *iso*amyl esters of *p*-aminobenzoic acid are also described in the patent: *methyl β-diethylaminoethyl-*p*-aminobenzoate monohydrochloride*, colourless lamellæ, m. p. 180°, soluble in water with neutral reaction; *propyl β-diethylaminoethyl-*p*-aminobenzoate hydrochloride*, m. p. 136°; n-*butyl β-diethylaminoethyl-*p*-aminobenzoate*, an oil, b. p. 214°/6 mm., forming a *monohydrochloride*, m. p. 127°; iso*butyl β-diethylaminoethyl-*p*-aminobenzoate hydrochloride*, m. p. 144°; and iso*amyl β-diethylaminoethyl-*p*-aminobenzoate hydrochloride*, m. p. 112°. G. F. M.

The Chloro-α-bromocinnamic Acids and their Affinity for Bromine. S. REICH, J. ARAUS, J. POTOK, and H. TEMPEL (*Helv. Chim. Acta*, 1920, **3**, 793—800).—In order to throw some light on various factors controlling the additive capacity of ethylenic linkings, the authors have studied the action of bromine on the three pairs of stereoisomeric chloro-α-bromocinnamic acids. These acids are obtained from the chlorobenzaldehydes, which are converted into *o*-, *m*-, and *p*-chlorocinnamic acids (m. p. 200°, 165°, 245°, respectively), then into the *o*-, *m*-, and *p*-chloro-αβ-dibromo-β-phenylpropionic acids (m. p. 181°, 176°, 187°, respectively), the latter being warmed with alcoholic potassium hydroxide (1 mol.) until the solution is no longer alkaline, when the solvent is evaporated, the concentrated solution is diluted, and fractionally precipitated by hydrochloric acid. The *cis*- and *trans*-modifications of the acids are both formed. As a rule, the latter separate first, and crystallisation from appropriate solvents affords a ready means of purifying the two forms. The characteristics of the acids and their derivatives are as follows. o-*Chloro-α-bromocinnamic acid*: *trans*-, needles, m. p. 161 (*methyl* ester, m. p. 51°; *aniline* salt, m. p. 134°); *cis*-, very long needles, m. p. 128°, passes into the *trans*-modification when exposed to sunlight or on the addition of a few drops of bromine to a solution in light petroleum (*methyl* ester, m. p. 61°; *aniline* salt, m. p. 123°). m-*Chloro-α-bromocinnamic acid*: *trans*-, small needles, m. p. 140° (*methyl* ester, m. p. 56°; *aniline* salt, m. p. 116°); *cis*-, small needles, m. p. 100° (*methyl* ester, m. p. 53°; *aniline* salt, m. p. 77°). p-*Chloro-α-bromocinnamic acid*: *trans*-, m. p. 256° (*methyl* ester, m. p. 82°; no aniline salt); *cis*-, m. p. 129° (*methyl* ester, m. p. 50°; *aniline* salt, m. p. 192°).

The affinity of the acids for bromine was studied by exposing equal weights in dishes around a central dish of bromine for eighteen hours in the dark, and weighing the products after exhausting in a desiccator. It is found that the *trans*-isomerides combine much less readily than the *cis*-modifications, and that, in the latter case, the position of the chlorine atom in the ring has very little influence. In the case of the *trans*-isomerides, however, the position of the chlorine atom is all-important, the influence being highly restraining in the ortho- and meta-positions, but very feeble in the para-position. J. C. W.

The Action of Sodium Hypochlorite on Amides. II. I. J. RINKES (*Rec. trav. chim.*, 1920, **39**, 704—710. Compare A., 1920, i, 322).—Phenylpropiolamide, when acted on by sodium hypochlorite in the presence of methyl alcohol, is converted directly into phenylacetonitrile. If, however, the amide is added to a cold aqueous solution of the hypochlorite, a *chloro*-derivative,

CPh:C·CO·NHCl,

m. p. 107° (decomp.), is obtained, which, when gently warmed with aqueous barium hydroxide, is converted into *barium phenyl-*

acetylenecarbamate, $(CPh\vdots C\cdot NH\cdot CO_2)_2Ba$, and this is decomposed by steam, giving phenylacetonitrile.

Styrylurethane, when oxidised in acetone solution with potassium permanganate, yields *αβ-dihydroxy-β-phenylethylurethane*, $OH\cdot CHPh\cdot CH(OH)\cdot NH\cdot CO_2Me$, which, when decomposed by sulphuric acid and distilled in a current of steam, yields α-hydroxyphenylacetaldehyde, giving an *oxime*, m. p. 158°, a *semicarbazone*, m. p. 222°, and an *osazone*, m. p. 152°. W. G.

Preparation of a Phenylated Aminohydrindenecarboxylic Acid. CHEMISCHE WERKE GRENZACH. AKT. GES. (D.R.-P. 325713; from *Chem. Zentr.*, 1920, iv, 558).—The product obtained by the condensation of α-hydrindone with isatin is treated with alkaline reducing agents. The condensation product is a colourless powder which does not melt below 295°. When it is treated with sodium in boiling amyl-alcoholic solution and the sodium salt is subsequently decomposed, a finely crystalline *phenylated aminohydrindenecarboxylic acid* (containing 76·43% C and 6·1% H), m. p. 180° after incipient discoloration and evolution of carbon dioxide at about 140°, is obtained; the *hydrochloride*, m. p. 205°, *acetyl* derivative, m. p. 287°, and *nitroso*-compound, platelets, m. p. 156°, are described. The acid is expected to find therapeutic application. H. W.

Synthesis of Sinapin. ERNST SPÄTH (*Monatsh.*, 1920, **41**, 271—285).—The author has succeeded in preparing synthetically a compound of the constitution proposed by Gadamer for sinapin (A., 1898, i, 38, 197), and finds it to be identical with the latter. Of the two products, choline and sinapic acid, yielded when sinapin is decomposed by alkali, the former is readily prepared. The method by which sinapic acid was synthesised is as follows. When methylated by means of methyl sulphate and sodium hydroxide, gallic acid yields gallic acid trimethyl ether (A., 1919, i, 548), which, when heated with hydrobromic acid, undergoes demethylation of the middle methoxyl group, with formation of 4-hydroxy-3:5-dimethoxybenzoic or syringic acid (Graebe and Martz, A., 1905, i, 702). The latter is converted by treatment with ethyl chloroformate and sodium hydroxide into carbethoxysyringic acid (Lepsius, A., 1914, i, 1072). Carbethoxysyringoyl chloride, which is thence easily obtainable, is transformed by means of hydrogen and palladinised barium sulphate (Rosenmund, A., 1918, i, 300) into carbethoxysyringinaldehyde, which, when hydrolysed by means of sodium hydroxide in a vacuum, yields quantitatively syringinaldehyde. When heated with malonic and glacial acetic acids, carbethoxysyringinaldehyde gives a benzylidenemalonic acid, which, in a vacuum at 220—230°, loses carbon dioxide and forms carbethoxysinapic acid. Hydrolysis of the latter by means of sodium hydroxide in a vacuum results in the formation of sinapic acid, identical with that prepared from natural sinapin.

The ordinary methods of esterification fail when applied to the esterification of the alcoholic hydroxyl group of choline by sinapic

acid. The desired end was, however, attained by taking advantage of the fact that compounds containing an alcoholic hydroxyl group may be readily benzoylated by means of benzoyl chloride in presence of a tertiary amine (Dennstedt and Zimmermann, A., 1886, 368). In place of choline, which does not exhibit suitable solubility, use was made of dimethylhydroxyethylamine,

$$OH\cdot CH_2\cdot CH_2\cdot NMe_2,$$

which, being a tertiary amine, favours the acylation of its own alcoholic hydroxyl group. The interaction of this amine and acetylsinapoyl chloride readily yields β-dimethylaminoethyl acetylsinapate; removal from the latter of the acetyl group gives the corresponding sinapate, and union of this with methyl iodide results in the quantitative formation of a quaternary iodide, which is found to be identical with that given by natural sinapin.

Thus, the various steps in the synthesis of sinapin are as shown in the following scheme:

$$CO_2H\cdot C_6H_2(OH)_3[3:4:5] \longrightarrow CO_2H\cdot C_6H_2(OMe)_3 \longrightarrow$$
$$CO_2H\cdot C_6H_2(OMe)_2\cdot OH[4] \longrightarrow CO_2H\cdot C_6H_2(OMe)_2\cdot O\cdot CO_2Et \longrightarrow$$
$$CHO\cdot C_6H_2(OMe)_2\cdot O\cdot CO_2Et \longrightarrow$$
$$C(CO_2H)_2\colon CH\cdot C_6H_2(OMe)_2\cdot O\cdot CO_2Et \longrightarrow$$
$$CO_2H\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot O\cdot CO_2Et \longrightarrow$$
$$CO_2H\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OH \longrightarrow$$
$$CO_2H\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OAc \longrightarrow$$
$$NMe_2\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OAc \longrightarrow$$
$$NMe_2\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OH \longrightarrow$$
$$NMe_3I\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OH.$$

Noteworthy is the intense yellow coloration obtained by addition of an alkaline reagent to an aqueous solution of a sinapin salt, even in high dilution (Gadamer, *loc. cit.*). The author's results show that the assumption that this is due to rearrangement into a quinonoid compound must be abandoned. Whereas pyrogallol 1:3-dimethyl ether, syringic acid, syringinaldehyde, carbethoxysinapic acid, and 3:5-dimethoxy-4-carbethoxybenzylidenemalonic acid are scarcely perceptibly coloured by dilute alkali hydroxide, sinapic acid gives a distinct, and ethyl and dimethylaminoethyl sinapates and sinapin salts a deep yellow, coloration. These phenomena are due to displacement of the ultraviolet absorption bands of benzene towards the red end of the spectrum by various substituents, continued displacement forcing these bands wholly into the visible spectrum, and giving a coloured compound. In the compounds here considered, this displacement is effected by the phenolic hydroxyl groups, especially after salt-formation, and by the residue, $\cdot CH\colon CH\cdot CO_2H$, particularly when this occupies the para-josition to a hydroxyl group. The fact that sinapic acid in alkaline solution produces a far less intense coloration than the ethyl ester is explained by the work of Baly and Schaefer (T., 1908, **93**, 1806), who found that, on esterification of the carboxyl group, the carbonyl of the residue, $\cdot CH\colon CH\cdot CO_2Et$, becomes more highly unsaturated, and hence more suitable for colour-formation than the carbonyl of the free carboxyl group.

Ethyl-carbonatosyringinaldehyde, $CHO{\cdot}C_6H_2(OMe)_2{\cdot}O{\cdot}CO_2Et$, forms white crystals, m. p. 100—101°.

4-*Ethyl-carbonato*-3 : 5-*dimethoxybenzylidenemalonic acid*,

$$C(CO_2H)_2{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}O{\cdot}CO_2Et,$$

forms a white, crystalline powder, m. p. 216—217° (decomp.).

Ethyl-carbonatosinapic acid,

$$CO_2H{\cdot}CH{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}O{\cdot}CO_2Et,$$

forms crystals, m. p. 174°.

Acetylsinapic acid (Gadamer, *loc. cit.*) has m. p. 188—193°. *Acetylsinapoyl chloride*, $C_{13}H_{13}O_5Cl$, forms white crystals, m. p. 142—144°.

β-Dimethylaminoethyl acetylsinapate aurichloride,

$$C_{17}H_{23}O_6N,HAuCl_4,H_2O,$$

forms an amorphous, yellow mass, which dries to a brown, brittle resin.

β-Dimethylaminoethyl sinapate, $C_{15}H_{21}O_5N$, forms yellow crystals, m. p. 127·5—128·5°.

Sinapin iodide, $C_{16}H_{24}O_5NI$, obtained either synthetically or from natural sinapin, has m. p. 185—186°; Gadamer (*loc. cit.*) gave m. p. 178—179°. The thiocyanate has m. p. 180—181°, and the hydrogen sulphate, m. p. 190—191°. T. H. P.

Sulphoxyl Compounds. XI. Derivatives of Hydrosulphamine. A. BINZ and E. HOLZAPFEL (*Ber.*, 1920, **53**, [*B*], 2017—2029).—Derivatives of hydrosulphamine (thiohydroxylamine) are readily obtained by treating the products of the condensation of formaldehyde sulphoxylate and aromatic amines with organic mono-substituted derivatives of hydrogen sulphide; thus with thioacetic acid, reaction appears to take place according to the scheme: $R{\cdot}NH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}OH + CH_3{\cdot}CO{\cdot}SH \longrightarrow R{\cdot}NH{\cdot}SAc + CH_2O + S + H_2O$, the somewhat unexpected course of the action being probably due to the tendency towards the formation of hydroxy-hydrogen sulphide, $H{\cdot}S{\cdot}OH$, which subsequently decomposes into sulphur and water. Mercaptans and phenyl mercaptan behave similarly to thioacetic acid towards aryliminomethylenesulphoxylate, and the reaction thus appears to be fairly general, although it does not invariably lead to such definite products. The hydrosulphamine derivatives are yellow substances which are stable in the absence of air, but are somewhat decomposed when exposed in the latter for a few days, and lose sulphur and the mercaptan component. They are unaffected by cold dilute acids and alkalis. Their melting points are 50° to 90° lower than those of the corresponding sulphur-free compounds.

Formaldehyde sulphoxylate reacts with thioacetic acid in aqueous methyl-alcoholic solution, with the formation of sodium acetate, sulphur, and formaldehyde. Diformaldehydesulphoxylic acid is decomposed by hydrogen sulphide, apparently with formation of sulphur.

A solution of formaldehyde sulphoxylate in water is converted by anthranilic acid at 70—80° into *anthranilomethylene sulphoxylate*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}ONa,2H_2O$, colourless

crystals, m. p. 96°, which is relatively stable when preserved in a vacuum, but slowly becomes oxidised on exposure to air. It is transformed by thioacetic acid in aqueous solution into S-*acetyl*-o-*hydrosulphaminobenzoic acid* [N-*thiolacetylanthranilic acid*], $CO_2H\cdot C_6H_4\cdot NH\cdot SAc$, m. p. 133°, by ethyl mercaptan into N-*ethyl thiolanthranilic acid*, m. p. 97—99°, and by phenyl mercaptan into N-*thiophenylanthranilic acid*, m. p. about 111°. *p*-Aminobenzoic acid and formaldehyde sulphoxylate give *sodium* p-*carboxyphenylaminomethylenesulphoxylate*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot S\cdot ONa,2H_2O,$$

from which p-N-*thiolacetylaminobenzoic acid*, m. p. 159—160°, and p-N-*ethylthiolaminobenzoic acid*, m. p. 121°, are derived.

o-*Phenylenediaminomethylenesulphoxylic acid*,

$$NH_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot S\cdot OH,$$

is obtained from *o*-phenylenediamine hydrochloride and formaldehyde sulphoxylate, and is transformed by thioacetic acid into diacetyl-*o*-phenylenediamine, m. p. 185—186°.

Formaldehyde sulphoxylate readily reacts with sodium arsanilate (atoxyl), but the product could not be isolated in substance, and was identified as the *sodium magnesium* salt,

$$AsO_3Mg\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot S\cdot ONa,2H_2O\,;$$

in solution, it is converted by thioacetic acid into a mixture of *thiolacetylaminophenyl-4-arsenic disulphide*,

$$AsS_2\cdot C_6H_4\cdot NH\cdot SAc,$$

m. p. 183° (decomp.), and *bisthiolacetylaminophenyl*-pp′-*arsenic sesquisulphide*,

$$AcS\cdot NH\cdot C_6H_4\cdot As\cdot S\overset{S}{\diagup\!\!\diagdown}S\cdot As\cdot C_6H_4\cdot NH\cdot SAc,$$

m. p. 159° (decomp.) after softening at 150°.

Anthranilomethylene sulphoxylate is converted by hydrogen sulphide in aqueous solution into (?) *bismethyleneanthranilotrisulphide*, $(CO_2H\cdot C_6H_4\cdot NH\cdot CH_2)_2S_3$, amorphous, yellow substance, m. p. 116°, which, after successive treatment with sodium hydroxide and acetic acid, and extraction with ether, is transformed into a *substance* of identical composition, m. p. 70° after softening at 40°. Hydrogen selenide and anthranilomethylene sulphoxylate give *dianthranilomethyleneoxyselenide sulphide*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot S\cdot Se\cdot O\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2H,$$

amorphous, yellow substance, m. p. 125° (decomp.) after softening at 50°, which, in alkaline solution, is readily decomposed by air, with the separation of red selenium. *p*-Phenylenediaminomethylenesulphoxylic acid hydrochloride is converted by hydrogen selenide into the *compound*, $C_{14}H_{18}O_5N_4S_3Se,HCl$, red precipitate, m. p. 183—184°, which, however, is possibly not uniform.

H. W.

Tetrachlorophenolphthalein. E. T. WHITING (*J. Amer. Chem. Soc.*, 1920, **42**, 2366—2368).—*Tetrachlorophenolphthalein*, m. p. 215°, is readily prepared by adding chlorine dissolved in glacial acetic acid to a solution of phenolphthalein in the same

solvent. It gives a *diacetate*, m. p. 117°, and closely resembles tetrabromophenolphthalein, both in its chemical and its physical properties. W. G.

Formation and Stability of *spiro*-Compounds. III. *spiro*-Compounds from *cyclo*Pentane. OSCAR BECKER and JOCELYN FIELD THORPE (T., 1920, **117**, 1579—1588).

Synthesis of 3 : 5-Dimethoxybenzaldehyde. F. MAUTHNER (*J. pr. Chem.*, 1920, [ii], **100**, 176—182).—m-*Dimethoxybenzyl alcohol*, $C_9H_{12}O_3$, needles, m. p. 47—48°, is produced by the reduction of 3:5-dimethoxybenzamide (compare Guareschi, A., 1875, 569; Max, A., 1891, 1219), but is most conveniently prepared from the aldehyde and potassium hydroxide. Its *ethyl ether*, $C_{11}H_{16}O_3$, b. p. 156—158°/11 mm., results from the electrolytic reduction of the acid in alcoholic sulphuric acid solution (compare Mettler, A., 1905, i, 436). 3:5-*Dimethoxybenzaldehyde*, $C_9H_{10}O_3$, m. p. 45—46°, from the alcohol by oxidation, is best prepared by reducing the acid chloride in xylene solution in presence of palladium–barium sulphate at 140° (compare Rosenmund, A., 1918, i, 300), and is characterised by the p-*nitrophenylhydrazone*, $C_{15}H_{15}O_4N_3$, red needles, m. p. 183—184°; the *oxime*, $C_9H_{11}O_3N$, needles, m. p. 119—120°; the *semicarbazone*, $C_{10}H_{13}O_3N_3$, needles, m. p. 177—178°. 3:4-*Dimethoxyphenyl* 3:5-*dimethoxystyryl ketone*, $C_{19}H_{20}O_5$, yellow needles, m. p. 103—104°, is obtained by condensing the aldehyde with acetylveratrone in presence of sodium hydroxide. J. K.

The Condensation of Benzoyl Chloride with Ethylene in the presence of Aluminium Chloride. JAMES F. NORRIS and HENRY B. COUCH (*J. Amer. Chem. Soc.*, 1920, **42**, 2329—2332).—The authors confirm Krapivin's work (A., 1910, i, 349) that a hydrogen atom in ethylene and one in benzene show similar reactivity. It seems probable, therefore, that unsaturated compounds containing a double bond can replace aromatic hydrocarbons in the Friedel-Crafts' synthesis. Ethylene condenses with benzoyl chloride in the presence of aluminium chloride to give phenyl vinyl ketone. W. G.

Melanin and Humus. I. The Formula of *p*-Benzoquinone; the Thermal Rearrangement in the Quinone Series; the Physiological Significance of Quinone Humus. HUGO STOLTZENBERG and MARGARETE STOLTZENBERG-BERGIUS (*Zeitsch. physiol. Chem.*, 1920, **111**, 1—31).—*The Decomposition of* p-*Benzoquinone with Boiling Water*.—*p*-Benzoquinone was heated in aqueous solution under a reflux condenser for five hours. The residue was extracted with methyl alcohol, and the *substance* thus obtained, $C_{12}H_8O_4$, was soluble in ammonia and alkali, from which it could be precipitated by acids. The *calcium* salt, $C_{48}H_{30}O_{16}Ca$, the *magnesium* salt, $C_{48}H_{30}O_{16}Mg$, the *iron* salt, $C_{144}H_{93}O_{48}Fe'''$, and the *copper* salt, $C_{24}H_{14}O_8Cu$, were obtained from it. On acetylating it with acetic anhydride for

twenty-four hours, a compound was obtained which showed that at least three of the oxygen atoms were present in the form of hydroxyl groups. The residue from the decomposition mixture, which was insoluble in methyl alcohol, was dissolved in $N/10$-sodium hydroxide and reprecipitated with hydrochloric acid; it had the empirical formula $C_{24}H_{12}O_9$.

Decomposition of p-*Benzoquinone by Heat.*—*p*-Benzoquinone was heated in a sealed tube at 165—185°, and the product extracted several times with boiling water and the residue treated with methyl alcohol. A substance, $C_{12}H_8O_4$, similar to that obtained by the decomposition with hot water was identified. From this a *tetra-acetate*, $C_{20}H_{16}O_8$, was prepared. The residue, insoluble in the methyl alcohol, yielded a substance which contained more carbon than the analogous compound from the hot-water decomposition. A *tetra-acetate*, $C_{20}H_{12}O_8$, which agreed with the derivative from a substance with the formula $C_{12}H_4O_4$, was prepared. On decomposing bromobenzoquinone by heat, a substance, $C_6H_3O_2Br$, was obtained, which was soluble in methyl alcohol, and another one, $C_{12}H_{6\cdot45}O_{4\cdot3}Br_{1\cdot37}$, which was not soluble in it. Similarly, substances with the formula $C_{12}H_7O_4Br_3$ and $C_{12}H_9O_8Br_5$, respectively, were obtained from dibromobenzoquinone by heat. The substances $C_{12}H_8O_4$ and $C_{24}H_{12}O_9$ were reduced with hydriodic acid and phosphonium iodide in a sealed tube at 200°. By fractional distillation, the following fractions were obtained: From $C_{12}H_8O_4$: 100—154°, $C_{12}H_{20}O_{0\cdot4}$; 155—200°, $S_{24}H_{38}$; residue, $C_{36}H_{46}$. From $C_{24}H_{12}O_9$: 127—140°, $C_{12}H_{20}$; 150—207°, $C_{24}H_{38}$; residue, $C_{24}H_{30}O$. On extracting with methyl alcohol the black wax obtained by reducing $C_{12}H_8O_4$, a substance, $C_{12}H_{10}O$, was received. Similarly, a substance, $C_{12}H_{10}O$, was yielded by extracting the black wax obtained as the reduction product of $C_{24}H_{12}O_9$. On oxidising $C_{12}H_8O_4$ with nitric acid, a product, $C_{12}H_8O_8$, was obtained. The bearing of the polymerisation of the quinones on the physiology of the animal cell is discussed.

S. S. Z.

Preparation of 2 : 4-Dihydroxy- and 2 : 4 : 4'-Trihydroxybenzophenone. The Hoesch Reaction. HENRY STEPHEN (T., 1920, **117**, 1529—1534).

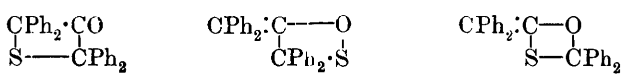
Ketens. XXXIV. Diphenylthioketen. H. STAUDINGER, G. RATHSAM, and F. KJELSBERG (*Helv. Chim. Acta*, 1920, **3**, 853—861).—Contrary to expectation, diphenylthioketen is such a very reactive substance that many likely methods of preparation were abandoned before it could be obtained, and even now it is only known as a polymeride. For example, no result of consequence was obtained in the action of phosphorus pentasulphide on diphenylketen, diphenylacetic acid, ethyl diphenylacetate, or *ethyl diphenylthiolacetate*, $CHPh_2 \cdot CO \cdot SEt$, m. p. 50° (prepared by the action of diphenylacetyl chloride on ethyl mercaptan in

alkaline solution). Similarly, no success was obtained by heating diphenylketen with carbon disulphide at 150° or allylthiocarbimide at 100°. Triphenylphosphinediphenylmethylene (A., 1920, i, 106), however, reacts with carbon disulphide at 60° to give triphenylphosphine sulphide and polymeric diphenylthioketen, thus, $PPh_3{:}CPh_2 + CS_2 = PPh_3S + CPh_2{:}CS$, whilst triphenylphosphine sulphide reacts with diphenylketen at about 80° to give triphenylphosphine oxide, the polymeride, and several by-products, including in one experiment thiobenzophenone.

Polymeric *diphenylthioketen* is a very stable, amorphous, yellow compound, m. p. 262°. It is insoluble in glacial acetic acid, whereas triphenylphosphine sulphide is soluble, and it forms a colloidal solution in benzene. When heated with aniline at 220—240°, it yields pale yellow *diphenylthioacetanilide*, m. p. 182°, if equimolecular proportions are used, or *diphenylacetyldiphenylamidine*, m. p. 111°, if an excess of aniline is taken, thus: $CPh_2{:}CS \longrightarrow CHPh_2{\cdot}CS{\cdot}NHPh \longrightarrow CHPh_2{\cdot}C({:}NPh){\cdot}NHPh$.

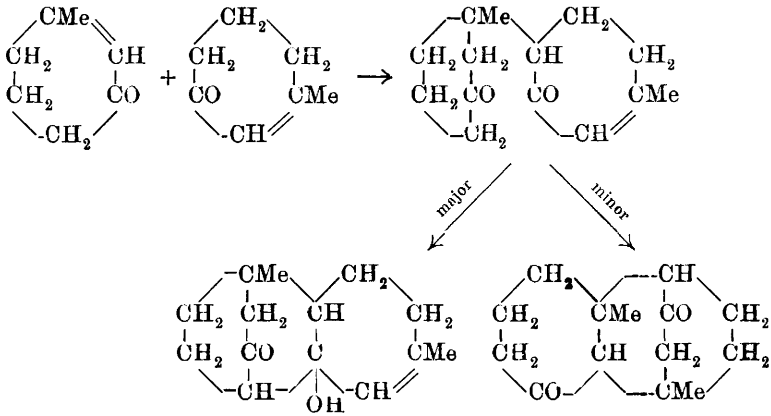
J. C. W.

Ketens. XXXV. Action of Diphenylketen on Thioketones. H. STAUDINGER [with H. W. KLEVER, ST. BEREZA, and A. CORVI] (*Helv. Chim. Acta*, 1920, **3**, 862—865).—Diphenylketen reacts with *pp'*-tetramethyldiaminothiobenzophenone when left in chloroform solution, giving tetramethyldiaminotetraphenylethylene (A., 1911, i, 876), thus: $(NMe_2{\cdot}C_6H_4)_2CS + CPh_2{:}CO \longrightarrow (NMe_2{\cdot}C_6H_4)_2C{<}^{\text{—S—}}_{CPh_2}{>}CO \longrightarrow (NMe_2{\cdot}C_6H_4)_2C{:}CPh_2 + COS$. Thiobenzophenone and *pp'*-dimethoxythiobenzophenone, however, form inert, white *compounds*, $C_{27}H_{20}OS$, m. p. 180—181°, and $C_{29}H_{24}O_3S$, m. p. about 120° (decomp.), which are resolved into the components when heated above the m. p., and give derivatives of the components when heated with aniline. These compounds probably correspond with one of the following formulæ:



J. C. W.

Polymerisation of Δ^2-*cyclo*Hexenones. L. RUZICKA (*Helv. Chim. Acta*, 1920, **3**, 781—792).—One or two examples of the polymerisation of Δ^2-*cyclo*hexenones by alkaline agents have already been described (Wallach, A., 1908, i, 424; Knoevenagel, A., 1899, i, 340), and it is now shown that the addition of about 1·5 mols. of sodamide to an ethereal solution of the ketone leads to the formation of dimerides in several other cases. The products yield mono-semicarbazones and mono-acetates, and, from certain analogies, the conclusion is drawn that the polymerisation proceeds according to the following scheme, taking the case of 3-methyl-Δ^2-*cyclo*hexenone:

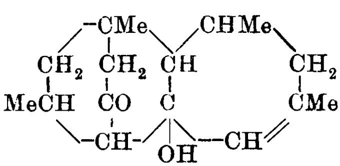


(I.) (II.)

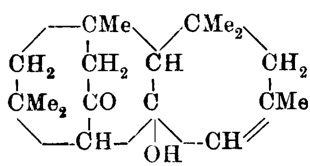
The *compound* (I) is a very viscous oil, b. p. 200—205°/12 mm., and contains probably about 10—15% of the diketone (II), since it forms a very sparingly soluble *disemicarbazone*, m. p. 246° (decomp.), as well as a freely soluble *semicarbazone*, m. p. 215° (decomp.), and a viscous, pale yellow *acetate*, b. p. 205°/12 mm. The compound may be hydrogenated in the presence of platinum-black, the *dihydro*-compound having b. p. 200°/12 mm., and its *acetate*, b. p. 215°/23 mm., the latter forming a *semicarbazone*, $C_{17}H_{27}O_3N_3$, m. p. 220°.

The *compound* (III) has m. p. 112°, b. p. 185°/11 mm., and corresponds, therefore, with Knoevenagel's description (*ibid.*). Its *acetate* is a pale yellow, viscous mass, b. p. 200—202°/12 mm.

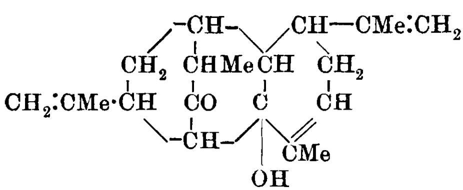
The *compound* (IV) is a yellow, viscous oil, b. p. 203—205°/



(III.)



(IV.)



(V.)

17 mm., 140°/0·2 mm., which forms a *semicarbazone*, m. p. 215° (decomp.), and an *acetate*, large prisms, m. p. 126°, b. p. 200°/12 mm.

The *compound* (V) is a pale yellow, viscous mass, b. p. 225°/12 mm., and its *semicarbazone* has m. p. 194—195° (decomp.), and *acetate*, b. p. 225°/11 mm. J. C. W.

Camphor. L. Ruzicka (*Helv. Chim. Acta*, 1920, **3**, 748—755).—I. *The Direct Production of Pure Bornylene.*—[With E. Rotheim.]—Camphor is converted into bornylamine by heating with ammonium formate under 60 atmos. pressure, and the base is transformed into bornyltrimethylammonium iodide, m. p. 245° (uncorr.) (Forster, T., 1899, **75**, 945, gave m. p. 250°). The corresponding hydroxide (I) is slowly decomposed at about 200°/0·125 mm., when the distillate is found to consist of bornylene (II), m. p. 111—112°, and bornyldimethylamine (III) in the pro-

$$C_8H_{14}\Big<\begin{matrix}CH\cdot NMe_3\cdot OH\\ |\\ CH_2\end{matrix} \quad \longrightarrow \quad C_8H_{14}\Big<\begin{matrix}CH\\ \|\\ CH\end{matrix} \quad + \quad C_8H_{14}\Big<\begin{matrix}CH\cdot NMe_2\\ |\\ CH_2\end{matrix}$$

(I.) (II.) (III.)

portions 2:1. This is apparently the first example of the transference of such a method of preparation from the alkaloid to the terpene series, and its success in the case of an unstable hydrocarbon like bornylene is noteworthy. The tertiary base (III) yields an isomeric methiodide, m. p. 278—279° (decomp.), which, in analogy with the usual borneol–*iso*borneol isomerism, is designated iso*bornyltrimethylammonium iodide.*

II. *The Sodium Condensation of Ethyl Homocamphorate.*—[With W. Kuhn.]—This section describes the successful application of another synthetic method, namely, the sodium condensation, in the closure of bicyclic terpene systems from esters of unicyclic dicarboxylic acids. Ethyl homocamphorate (I) is boiled with sodium in xylene, and thus converted into ethyl camphocarboxylate (II), which changes into camphor when boiled with hydrochloric acid. The yield of camphor from the initial ester is 68%.

The preparation of the ester (I) was based on Haller and Minguin's process (A., 1890, 638). Ethyl camphocarboxylate (II)

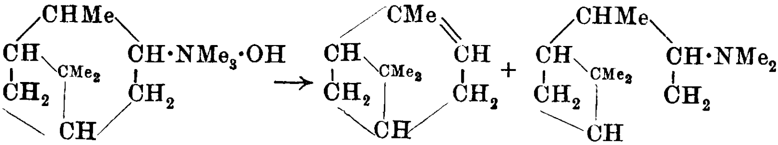
$$C_8H_{14}\Big<\begin{matrix}CO_2Et\\ CH_2\cdot CO_2Et\end{matrix} \quad \underset{NaOEt}{\overset{Na}{\rightleftarrows}} \quad C_8H_{14}\Big<\begin{matrix}CO\\ |\\ CH\cdot CO_2Et\end{matrix}$$

(I.) (II.)

(from camphor) is heated with a solution of sodium in alcohol in an autoclave at 200°, and thus converted into a mixture of the desired ester (I) and the acid ester (3-carbethoxy-2:2:3-trimethyl*cyclo*pentylacetic acid), $C_8H_{14}\Big<\begin{matrix}CO_2Et\\ CH_2\cdot CO_2H\end{matrix}$, m. p. 75°, with a little camphor. The solvent is removed, the residue is boiled with concentrated hydrochloric acid to convert the normal ester into the acid ester, and this is dissolved in sodium hydroxide, freed from camphor, and finally isolated and re-esterified. J. C. W.

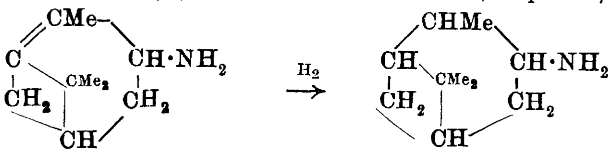
Pinene. I. Partial Synthesis of Pinene from a Pinene Derivative. L. Ruzicka and H. Trebler (*Helv. Chim. Acta*, 1920, **3**, 756—761).—As another example of the decomposition of quaternary ammonium hydroxides in the terpene series (compare

preceding abstract), the conversion of pinocamphyltrimethylammonium hydroxide (I) into pure α-pinene (II) and pinocamphyldimethylamine (III) is now described. The required



(I.) (II.) (III.)

material is obtained as follows. A mixture of pinene, glacial acetic acid, and ethyl nitrite is treated with alcoholic hydrogen chloride, the pinene-nitrosochloride is reduced by means of zinc dust and acetic acid to pinylamine (IV) (and pinocamphone), and this base is hydrogenated in the presence of platinum-black. The pinocamphylamine (V) so formed is a mobile oil, b. p. 90°/12 mm.,



(IV.) (V.)

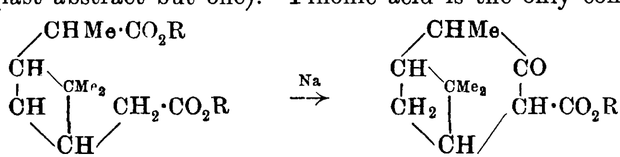
of different stereoisomeric relationships from the bases described by Tilden (T., 1906, **89**, 1560) and Wallach (A., 1901, i, 90), as the following table of m. p.'s of derivatives shows:

	Acetate.	Picrate.	Hydrochloride.	Carbamide.
Tilden	108—110°	208°	above 300°	204°
Wallach	120°	—	—	204°
Ruzicka	112°	217°	about 340°	170°

The *pinocamphyltrimethylammonium iodide*, hitherto unknown, forms colourless scales, m. p. 255°. An *isomeride*, m. p. 300—301°, is yielded by the pinocamphyldimethylamine (III), obtained by the distillation of the ammonium hydroxide.

J. C. W.

Pinene. II. Attempts to Prepare Homopinocamphoric Acid from Pinonic Acid. Conversion of Pinonic Acid into Tetrahydrocarvone. L. Ruzicka and H. Trebler (*Helv. Chim. Acta*, 1920, **3**, 762—781).—As a new process for building up the tetrocean system of pinene, the sodium condensation of ethyl homopinocamphorate (I) would seem to offer many advantages, such a synthetic method having already been successful in similar case (last abstract but one). Pinonic acid is the only conceivable



(I.)

source of the required compound (I) at present, but two different methods for converting it into homopinocamphoric acid have been unsuccessful, whilst a third is still being investigated. A few improvements in Baeyer's process for oxidising pinene to pinonic acid are described (A., 1896, i, 245).

Scheme I.—This is outlined as follows:

$$\underset{\text{(II.)}}{C_6H_{10}{<}\begin{matrix}COMe\\CH_2\cdot CO_2Et\end{matrix}} \rightarrow \underset{\text{(III.)}}{C_6H_{10}{<}\begin{matrix}CHMe\cdot OH\\CH_2\cdot CO_2Et\end{matrix}} \rightarrow C_6H_{10}{<}\begin{matrix}CHMeCl\\CH_2\cdot CO_2Et\end{matrix}$$

$$\downarrow$$

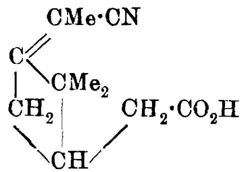
$$\underset{\text{(I.)}}{C_6H_{10}{<}\begin{matrix}CHMe\cdot CO_2Et\\CH_2\cdot CO_2Et\end{matrix}} \leftarrow C_6H_{10}{<}\begin{matrix}CHMe\cdot CN\\CH_2\cdot CO_2Et\end{matrix}$$

Ethyl pinonate (II) is obtained best by boiling the acid with dilute alcoholic hydrogen chloride, and its *semicarbazone* has m. p. 136°. Reduction to ethyl pinolate (III) is very easily effected by means of hydrogen and platinum-black, but the subsequent chlorination and introduction of the cyanogen group have so far been a failure.

Scheme II.—Here the idea was to convert the cyanohydrin of pinonic acid (IV) into the nitrile (V) by means of phosphorus pentachloride, but the reactions of the product prove it to have the formula (VI). Pinonic acid *cyanohydrin* (IV) forms colour-

$$C_6H_{10}{<}\begin{matrix}CMe{<}\begin{matrix}OH\\CN\end{matrix}\\CH_2\cdot CO_2H\end{matrix}$$

(IV.)



(V.)

$$CN\cdot CMe{:}CH\cdot CH_2\cdot CH{<}\begin{matrix}CMe{:}CH_2\\CH_2\cdot CO_2H\end{matrix}$$

(VI.)

less crystals, m. p. 94°, and is hydrolysed by aqueous hydrochloric acid to the keto-lactone, $COMe\cdot CH_2\cdot CH_2\cdot \overset{CMe_2-O}{\underset{|}{C}}H\cdot CH_2{>}CO$ (Baeyer, A., 1896, i, 308). The *ethyl* ester of pinonic acid cyanohydrin, b. p. 150—152°/0·4 mm., is obtained by treating the cyanohydrin with ethereal thionyl chloride at a low temperature, and then boiling with alcohol. Using phosphorus pentachloride at below 5°, the above unusual transformation takes place, and the product may be isolated as *ethyl β-cyano-ζ-methyl-$\Delta^{\beta\zeta}$-heptadiene-ε-acetic acid* (compare VI), a pale yellow oil, b. p. 120—130°/0·3 mm. This is hydrolysed by aqueous-alcoholic potassium hydroxide to *β-carboxy-ζ-methyl-$\Delta^{\beta\zeta}$-heptadiene-ε-acetic acid*,

$$CO_2H\cdot CMe{:}CH\cdot CH_2\cdot CH{<}\begin{matrix}CMe{:}CH_2\\CH_2\cdot CO_2H\end{matrix},$$

which is a viscous mass, and forms a *methyl* ester, mobile oil, b. p. 115°/0·3 mm., and *ethyl* ester, b. p. 115°/0·3 mm. When the

crude acid is heated with acetic anhydride at 180° for ten hours, it is converted into the acetate of carvacrol, the phenol being isolated after saponifying the product. The two esters absorb two molecular proportions of hydrogen in the presence of platinum-black, giving the esters of *α-methyl-δ-isopropylpimelic acid*, $CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$. The *methyl* ester is a mobile oil, b. p. 108°/0·3 mm., and the *ethyl* ester has b. p. 115°/0·3 mm., whilst the acid is a viscous mass. The product obtained by boiling the esters with sodium in xylene, or by distilling the lead salt, is tetrahydrocarvone, which proves their constitution. J. C. W.

Constituents of Resins. VI. Amyrins from the Elemi Resin of Manila : I. Separation of the Amyrins. ALOIS ZINKE, ALFRED FRIEDRICH, and ALEXANDER ROLLETT (*Monatsh.*, 1920, **41**, 253—270).—Methods for separating the α- and β-amyrins of elemi resin have been given by Vesterberg (A., 1887, 733; 1891, 615; 1892, 288, 290) and by Tschirsch and Cremer (A., 1902, i, 812). The authors find that crude amyrin benzoate may be separated, by fractional crystallisation from acetone, into α- and β-amyrin benzoates, the α-compound being subsequently purified by alternate treatments with ethyl acetate and acetone. The α- and β-benzoates thus isolated, and also the corresponding amyrins, exhibit the properties ascribed to them by Vesterberg.

α-Amyrin benzoate, $C_{37}H_{54}O_2$, m. p. 191° (uncorr.), $[\alpha]_D^{10}$ +94·57° (in chloroform), D^{18} 1·096, forms rhombic crystals [KARL SCHULZ: $a:b:c=2·721:1:0·973$], and, when treated with bromine in acetic acid solution, yields *bromo-α-amyrin benzoate*, $C_{37}H_{53}O_2Br$, which forms crystals, m. p. 229° (uncorr.), and is almost insoluble in cold concentrated sulphuric acid, but when heated with the latter gives a brown coloration and a slight green fluorescence. α-Amyrin, m. p. 183—184° (uncorr.), dissolves in the hot in concentrated sulphuric acid to a lemon-yellow solution showing green fluorescence.

The isomeric β-amyrin benzoate, m. p. 229—230° (uncorr.), $[\alpha]_D^{10}$ +100·2° (in chloroform), crystallises in almost rectangular plates belonging to the monoclinic system [KARL SCHULZ: $a:b:c=5·576:1:1·789$; $\beta=89°54'$]. By bromine in acetic acid solution, it is converted into *dibromo-β-amyrin benzoate*,

$$C_{37}H_{52}O_2Br_2,$$

which crystallises mostly in slender needles, but sometimes in spherical aggregates, m. p. 211—212° (uncorr.). β-Amyrin, m. p. 193—194°, dissolves in the cold in concentrated sulphuric acid, giving a lemon-yellow solution with green fluorescence.

T. H. P.

Chemistry and Pharmacology of Digitoxin and its Decomposition Products. M CLOETTA (*Arch. exp. Path. Pharm.*, 1920, **88**, 113—157. Compare Cloetta and Fischer, A., 1906, ii, 474).—A new method is described for the preparation of pure, crystallised digitoxin from *Digitalis* leaves, the product obtained differing markedly from any of those previously described

as digitoxin or digitalin, which must have been impure. Digitoxin crystallises in characteristic, narrow plates, m. p. 252°, and a number of analyses give the mean percentages of carbon and hydrogen as 64·19 and 8·66 respectively. Cryoscopic determinations of the molecular weight in glacial acetic acid, in which the digitoxin must not remain long dissolved, give the approximate value 800.

When heated in a high vacuum, digitoxin yields a volatile *compound*, $C_8H_{14}O_4$, which crystallises in long, white needles, m. p. 116° (corr.), sublimes at temperatures above 100°, and yields a neutral aqueous solution, which does not reduce Fehling's solution. This compound is pharmacologically indifferent, responds to Keller's reaction with a more intense bluish-green coloration of the acetic acid than is given by pure digitoxose, combines with iodine or bromine, and gives the normal molecular weight in freezing acetic acid.

The residue remaining after removal of the preceding volatile compound from digitoxin is termed *digitan*, and separates from aqueous alcohol in small, highly refractive balls. According to the analytical results, and to those of cryoscopic measurements in acetic acid, the formula of digitan is $C_{36}H_{56}O_{10}$. It gives Keller's reaction, 1 mg. of digitan yielding the same intensity of the blue coloration as 0·7 mg. of digitoxin. The pharmacological action of digitan towards both frogs and warm-blooded animals is identical with that of digitoxin. By aqueous-alcoholic hydrochloric acid, digitan (1 mol.) is decomposed, giving digitoxigenin (1 mol.) and digitoxose (2 mols.).

Hydrolysis of digitoxin (1 mol.) by acids under various conditions yields always digitoxigenin (1 mol.), digitoxose (2 mols.), and an oily compound, $C_8H_{14}O_4$ (?) (1 mol.), which corresponds with the volatile compound formed when digitoxin is heated in a vacuum, and may be obtained from this by treatment with acid; the oily compound responds strongly to the digitoxose reaction, gives no sugar reaction, and is pharmacologically indifferent.

On application of Keller's reaction to pure digitoxigenin, m. p. 245°, a yellow ring is first formed, the acetic acid then assuming a pale green coloration; when the liquid is shaken, it becomes permanently emerald-green and fluorescent, whereas with impure preparations a red coloration results. Molecular weight determinations in freezing acetic acid lead to the formula $C_{24}H_{36}O_4$ for digitoxigenin. The latter exerts a distinct effect on the heart, but this differs, both qualitatively and quantitatively, from that produced by digitoxin; it acts also as a convulsive poison.

Anhydrodigitoxigenin, $C_{24}H_{34}O_3$, obtained by the action of acids in the hot on digitoxigenin, or by more profound decomposition of digitoxin by acid, forms small needles, m. p. 184° (compare Kiliani, A., 1899, i, 71). The hydrolysis of digitoxin may be so controlled that either digitoxigenin or anhydrodigitoxigenin alone is formed, the reaction proceeding quantitatively. Anhydrodigitoxigenin has no effect on the heart, but still produces con-

vulsions. Since this compound does not exhibit the typical digitalis action, the formation of the anhydride must be accompanied by loss of a reactive group.

Dixgenic acid, $C_{24}H_{38}O_5$, m. p. 243—244°, prepared by heating digitoxigenin with aqueous-alcoholic sodium hydroxide, and also sodium dixgenate, possess no pharmacological properties. Attempts to effect alteration in digitoxigenin by treatment with dilute permanganate or hydrogen peroxide solution, and thus obtain products with modified pharmacological action, were unsuccessful.

The digitoxose obtained by hydrolysing digitoxin agrees in properties with Kiliani's product (A., 1896, i, 59; 1897, i, 95; 1899, i, 70, 932), except that it has m. p. 107°, and not 101°.

The foregoing results indicate for digitoxin the formula $C_{44}H_{70}O_{14}$, the decomposition of digitan by acid, with formation of digitoxigenin and digitoxose, being represented by the equation $C_{36}H_{56}O_{10} + 2H_2O = C_{24}H_{36}O_4 + 2C_6H_{12}O_4$, and the primary acid decomposition of digitoxin by the equation $C_{44}H_{70}O_{14} + 2H_2O = C_{24}H_{36}O_4 + 2C_6H_{12}O_4 + C_8H_{14}O_4$ (?).

Pentabenzoyldigitoxin crystallises in rosettes of small rods sintering at 145°, m. p. 156—158°, and is without pharmacological action. Condensation of digitoxin with phenylcarbimide yields a white, non-crystalline *compound*, which contains two phenylcarbimide residues, and has a pharmacological action equal to one-half or two-thirds of that of digitoxin itself. Treatment of digitoxin with stearoyl chloride in pyridine solution yields a *compound*, which crystallises in slightly refracting spherules, contains five stearic acid residues, and is devoid of pharmacological action.

Digitan yields a crystalline benzoyl derivative, which is inactive pharmacologically.

In the substitution of the five hydroxyl groups of the digitoxin molecule, it may be assumed that two acid residues are introduced in each of the two sugar molecules, and the fifth into the digitoxigenin part of the molecule. Benzoylation of digitoxigenin yields indefinite results, but acetylation gives *monoacetyldigitoxigenin*, which crystallises in transparent, colourless prisms, m. p. 219—220°, and exerts the convulsive effect, but no action on the heart. It is therefore evident that the characteristic digitalis effect and the convulsive action of digitoxigenin are not due to the same groupings.

Commercial preparations of crystalline digitoxin are found to possess widely differing compositions and pharmacological effects.

T. H. P.

Hyenanchin and other Constituents of *Hyenanche globosa*. THOMAS ANDERSON HENRY (T., 1920, **117**, 1619—1625).

The Coumaranone Series. I. The Preparation of 4-, 5-, and 6-Methylcoumaran-2-ones, and some Derivatives of *o*-, *m*-, and *p*-Tolyloxyacetic Acids. LUCY HIGGINBOTHAM and HENRY STEPHEN (T., 1920, **117**, 1534—1542).

The Chroman Series. I. ANNIE GREENWOOD and MAXIMILIAN NIERENSTEIN (T., 1920, **117**, 1594—1599).

"Furol Green." OTTO FISCHER and LUDWIG GRAHL (*J. pr. Chem.*, 1920, [ii], **100**, 159—167).—The yield of the leuco-base of "furol green," colourless needles, m. p. 83°, from the condensation of furfuraldehyde with dimethylaniline in presence of zinc chloride (A., 1881, 587) is about 30% under the conditions now described. The *dihydrobromide*, $C_{21}H_{24}ON_2,2HBr$, yellow leaflets; the *dihydriodide*, $C_{21}H_{24}ON_2,2HI$, yellow leaflets; the *acid sulphate*, $2C_{21}H_{24}ON_2,3H_2SO_4$, colourless needles, decomp. 140°; the *dipicrate*, $C_{27}H_{25}O_8N_5$, needles with a copper lustre; the *dipicrolonate*, $C_{21}H_{24}ON_2,2C_{10}H_8O_5N_4$, a brownish-yellow powder, m. p. 174°, decomp.; the *dimethiodide*, $C_{21}H_{24}ON_2,2MeI$, yellow crystals, decomp. *ca.* 210°. The corresponding *dye*, from the leuco-base by means of lead peroxide, was analysed in the form of its *bromide*, $C_{21}H_{23}ON_2Br,4H_2O$, silky, green needles; the *iodide*, $C_{21}H_{23}ON_2I,4H_2O$, forms green needles; the carbinol base forms brown flocks. *Tetraethyldiaminofuryldiphenylmethane*, $C_{25}H_{32}ON_2$, white needles, m. p. 80—81°, gives a *dihydriodide*, $C_{25}H_{34}ON_2I_2$, colourless aggregates, decomp. *ca.* 145°; a *dipicrate*, $C_{25}H_{32}ON_2,2C_6H_3O_7N_3$, light yellow needles, decomp. *ca.* 180°; a *dipicrolonate*, $C_{45}H_{48}O_{11}N_{10}$, a greenish-yellow powder, decomp. 155—156°; a *dimethiodide*, $C_{27}H_{38}ON_2I_2$, yellow prisms; and a *diethiodide*, $C_{29}H_{42}ON_2I_2$, white needles. The corresponding dye ("furol-green Ae") gives an *iodide*, $C_{25}H_{31}ON_2I$, green prisms, decomp. *ca.* 182—185°, and a *picrate*, $C_{31}H_{33}O_8N_5$, dark bronze crystals. The carbinol base forms brown, amorphous flocks. These dyes colour silk, cellulose, and wool a brilliant yellowish-green, but in the last case the stability to light is only slight. J. K.

The Reaction between Magnesium Phenyl Bromide and the Esters or Anhydride of Phthalic Acid. LLOYD B. HOWELL (*J. Amer. Chem. Soc.*, 1920, **42**, 2333—2337).—It is shown that the different results obtained by Guyot and Catel (A., 1905, i, 226) and Shibata (T., 1909, **95**, 1449) in the condensation of excess of magnesium phenyl bromide with phthalic esters or anhydride are due to the different methods used for isolating the products. If the product is isolated, after hydrolysis, by crystallisation from ether or benzene, 2-hydroxy-1:1:2-triphenyl-1:2-dihydrobenzofuran, m. p. 118° (corr.), is obtained (compare Guyot and Catel, *loc. cit.*). If, however, the product is isolated by distillation under reduced pressure, the phthalan derivative, m. p. 192—193°, described by Shibata (*loc. cit.*) is obtained. Further, if the compound, m. p. 118°, is distilled under reduced pressure, the compound, m. p. 192—193°, is obtained. W. G.

Action of Aliphatic Diazo-compounds on Thioketones. H. STAUDINGER and JOSEPH SIEGWART (*Helv. Chim. Acta*, 1920, **3**, 833—840).—Thiobenzophenone and diphenyldiazomethane react together very vigorously, even when diluted with light petroleum, the product being *tetraphenylethylene sulphide*, white crystals, which decompose at about 175° into tetraphenylethylene and sulphur. The reaction apparently proceeds according to the scheme:

$$CSPh_2 + CPh_2N_2 \longrightarrow S{<}\begin{array}{l}CPh_2{\cdot}CPh_2\\ N{=\!=}N\end{array} \xrightarrow{-N_2} S{<}\begin{array}{l}CPh_2\\ CPh_2\end{array} \xrightarrow{-S} \begin{array}{c}CPh_2\\ \Vert\\ CPh_2\end{array}$$

Diphenylenediazomethane reacts almost as readily, giving *diphenyl-diphenylene-ethylene sulphide*, $S{<}\begin{array}{l}CPh_2\\ C(C_6H_4)_2\end{array}$, which melts and decomposes at 190—200, forming diphenyldiphenylene-ethylene.

p-Methoxythiobenzophenone reacts less readily than the unsubstituted compound with diphenyldiazomethane, and *pp'*-tetramethyldiaminothiobenzophenone is still more sluggish. *Diphenyl-*pp'*-dimethoxydiphenylethylene sulphide* forms white needles, m. p. 100° (decomp.), and *diphenyl-*pp'*-tetramethyldiaminodiphenylethylene sulphide* crystallises in pale yellow needles, m. p. 164—165°.

Comparing the reactivity of various aliphatic diazo-compounds towards thiobenzophenone, it is stated in a general way that those with no carbonyl groups react best, those with one carbonyl group are less reactive, and those with two such groups, such as ethyl diazomalonate, are quite indifferent. Regarding the behaviour of different thiocarbonyl derivatives towards one diazo-compound, it is found that aromatic thioketones are most reactive, whilst such substances as ethyl dithiobenzoate, thiobenzanilide, and thiocarbamide are very indifferent. Strange to say, the above substituted thiobenzophenones are less active than the unsubstituted compound, in spite of the presence of groups which increase the reactivity of ordinary benzophenone. J. C. W.

Action of Thio-acid Chlorides on Aliphatic Diazo-compounds. H. STAUDINGER and JOSEPH SIEGWART [with E. ANTHES, H. BOMMER, and O. GERHARDT] (*Helv. Chim. Acta*, 1920, **3**, 840—852).—Thiocarbonyl chloride and thiobenzoyl chloride react most vigorously with aliphatic diazo-compounds, especially those without carbonyl groups, but the attack takes place at the ·CS group, and not the chlorine atom, as in the case of ordinary acid chlorides. The products, therefore, are quite different, and depend on the nature of the diazo-compound.

Thiocarbonyl chloride reacts so violently with diphenyldiazomethane and diphenylenediazomethane that the reagents must be diluted with light petroleum and mixed in the cold. The products are *αα-dichloro-ββ-diphenylethylene sulphide*, white needles, m. p. 89—90°, and *dichlorodiphenylene-ethylene sulphide*.

$S<\begin{matrix}CCl_2\\ |\\ C(C_6H_4)_2\end{matrix}$, m. p. 97°, which decompose very readily into αα-dichloro-ββ-diphenylethylene, m. p. 80°, and *dichlorodiphenylene-ethylene*, $CCl_2{:}C(C_6H_4)_2$, pale yellow needles, m. p. 129—130°. In these compounds, the chlorine atoms are very inert.

Benzoylphenyldiazomethane, however, gives a *compound*,

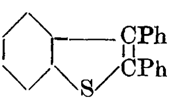
$$S<\begin{matrix}CCl_2\cdot CPh\\ \quad\ \ \|\\ O\text{——}CPh\end{matrix},$$

colourless crystals, m. p. 55—57°, in which the chlorine atoms are very reactive. Moisture alone, or moist alcohol, suffices to change it into the stable *compound* (I), m. p. 76—78°, which yields deoxybenzoin when heated with alcoholic potassium hydroxide, thus:

$$\text{(I) } S<\begin{matrix}CO\cdot CPh\\ \quad\ \ \|\\ O\text{—}CPh\end{matrix} \rightarrow \begin{matrix}CPh\cdot CO_2H\\ \|\\ CPh\cdot OH\end{matrix} \rightarrow \begin{matrix}CHPh\cdot CO_2H\\ |\\ COPh\end{matrix} \rightarrow CH_2Ph\cdot COPh.$$

Aniline likewise removes the chlorine atoms, giving the *compound*, $S<\begin{matrix}C({:}NPh)CPh\\ \qquad\quad\ \|\\ O\text{————}CPh\end{matrix}$, in white crystals, m. p. 129—130°.

Thiobenzoyl chloride and diphenyldiazomethane form *chlorotriphenylethylene sulphide*, m. p. 70—71°, which loses hydrogen chloride when heated at 100°, the product being probably *diphenylbenzthiophen* (annexed formula), this crystallising in colourless needles, m. p. 114°. Diphenylenediazomethane yields *chlorophenyldiphenylene-ethylene sulphide*, $S<\begin{matrix}CPhCl\\ |\\ C(C_6H_4)_2\end{matrix}$, colourless needles, m. p. 125—126°, which changes into *chlorophenyldiphenylene-ethylene*, pale yellow crystals, m. p. 119—120°, when heated at 150—180°, and into a yellow *compound*, $C_{20}H_{14}S$, m. p. 237—238°, when boiled with alcohol.



Methyl diazoacetate and thiobenzoyl chloride react readily, the *product*, m. p. 102°, having, most probably, the formula

$$\begin{matrix}CPh\cdot S\\ \|\qquad\\ N\text{—}N\end{matrix}\!\!>C\cdot CO_2Me.$$

J. C. W.

Syntheses in the Cinchona Series. VI. Aminoazo- and Hydroxyazo-dyes derived from certain 5-Amino-cinchona Alkaloids and their Quinoline Analogues. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1920, **42**, 2278—2286. Compare A., 1920, i, 633, 634).—5-Aminodihydroquinine couples readily with diazotised aromatic amines to form crystalline azo-dyes in which the amino-group is very labile, boiling for a few minutes with dilute mineral acid being sufficient to replace the amino-group by the hydroxyl group. Similar results were obtained with 5-aminodihydroquinidine and 5-aminoethyldihydrocupreine (amino-optochin). The lability of the amino-group

is apparently due largely to the quinoline nucleus in the molecule, as similar results were obtained, although somewhat less readily, with the azo-derivatives from 5-aminoquinoline. The presence of a methoxy- or ethoxy-group in position 6 also contributes markedly to the lability of the amino-groups in these compounds, as the amino-group in benzeneazo-5-amino-6-methoxyquinoline is much more readily replaced by hydroxyl than it is in the case of benzeneazo-5-aminoquinoline.

5-*Amino-8-benzeneazodihydroquinine*, m. p. 155—157° (decomp.), readily gave 5-*hydroxy-8-benzeneazodihydroquinine*, m. p. 145—148° (decomp.). 5-*Amino*-8-p-*sulphobenzeneazodihydroquinine* gave the corresponding 5-*hydroxy*-derivative. 5-*Amino*-8-p-*methoxybenzeneazodihydroquinine*, m. p. 150—153°, gave the 5-*hydroxy*-derivative. 5-*Amino*-8-p-*ethoxybenzeneazodihydroquinine*, m. p. 202—203° (decomp.), gave its 5-*hydroxy*-derivative. 5-*Amino-8-benzeneazodihydroquinidine*, m. p. 140—145° (decomp.), gave the 5-*hydroxy*-derivative, and 5-*amino-8-benzeneazoethyldihydrocupreine*, m. p. 150—155° (decomp.), gave 5-*hydroxy-8-benzeneazoethyldihydrocupreine*, m. p. 90·5°.

5-*Amino-8-benzeneazoquinoline*, m. p. 209—211°, required much longer heating with hydrochloric acid for its conversion into 5-*hydroxy-8-benzeneazoquinoline*, m. p. 164—165°, whereas 5-*amino-6-methoxy-8-benzeneazoquinoline*, m. p. 163—164°, readily yielded 5-*hydroxy*-6-*methoxy*-8-*benzeneazoquinoline*, m. p. 181—183°.

On reduction, the new cinchona- and quinoline-dyes yielded amino-compounds, in which interesting relationships have been observed in the replacement of the amino-group by hydroxyl.

W. G.

Aristochin and Optochin Nitrates. L. VAN ITALLIE and M. LE COULTRE (*Pharm. Weekblad*, 1920, **57**, 741): A. L. W. E VAN DER VEEN (*ibid.*, 742).—The first note describes the preparation of the nitrates of optochin (*B*, $2HNO_3$) and aristochin (*B*, $4HNO_3$), respectively, by the addition of excess of dilute nitric acid to the bases, or by the addition of sodium nitrate or dilute nitric acid to solutions of the bases in acetic or sulphuric acid. The nitrates, which are only sparingly soluble, separate in crystals, which have been examined microscopically by van der Veen. The two substances are very similar, possess rhombic symmetry, and, when examined between crossed Nicols in sections perpendicular to an optic axis, show colours by reason of their high dispersion.

S. I. L.

Synthesis of Ephedrine, ψ-Ephedrine, their Optical Antipodes and Racemic Compounds. ERNST SPÄTH and RUDOLF GÖHRING (*Monatsh.*, 1920, **41**, 319—338).—Although the investigations of Ladenburg and of Ernst Schmidt and his pupils have shown that ephedrine and ψ-ephedrine are stereoisomeric and have the formula OH·CHPh·CHMe·NHMe, these alkaloids have not yet been synthesised (compare Fourneau, A., 1905, i, 57;

Eberhard, A., 1915, i, 834). The synthesis has been effected by the authors by means of the following series of reactions:

(1) $CH_3 \cdot CH_2 \cdot CHO + Br_2 = CHMeBr \cdot CHO + HBr$;
(2) $CHMeBr \cdot CHO + HBr + MeOH = CHMeBr \cdot CHBr \cdot OMe + H_2O$;
(3) $CHMeBr \cdot CHBr \cdot OMe + MgPhBr = OMe \cdot CHPh \cdot CHMeBr + MgBr_2$;
(4) $OMe \cdot CHPh \cdot CHMeBr + NH_2Me = OMe \cdot CHPh \cdot CHMe \cdot NH_2MeBr$;
(5) $OMe \cdot CHPh \cdot CHMe \cdot NHMe + HBr = OH \cdot CHPh \cdot CHMe \cdot NHMe + CH_3Br$.

Reaction (1) proceeds moderately readily at a low temperature, and, in accordance with the results obtained by Franke with *iso*butaldehyde (A., 1900, i, 428) and by previous investigators with other aliphatic compounds, the bromine atom enters in the α-position to the carbonyl group; the α-bromopropaldehyde is obtained, not in the pure state, but as its viscous additive compound with hydrogen bromide, this having a penetrating odour. (2) Passage of hydrogen bromide through a mixture of the crude α-bromopropaldehyde and methyl alcohol at a low temperature yields $\alpha\beta$-dibromo-α-methoxypropane, which was isolated almost pure. Reaction (3) gave a 50% yield of β-bromo-α-methoxyphenylpropane, and when this was treated with anhydrous methylamine at 100°, 28% of it underwent reaction (4), the remainder suffering loss of hydrogen bromide, with probable formation of the compound, $OMe \cdot CPh:CHMe$; the latter, owing to its ready hydrolysability and its tendency to rearrangement, was largely transformed into phenyl ethyl ketone. Preparation of the compound, $OMe \cdot CHPh \cdot CHMeBr$, was necessary, since, as was found by Mannich (A., 1910, i, 411) for other halogenohydrins, the action of methylamine on the methoxyl-free bromohydrin might result first in loss of hydrogen bromide and formation of the oxide, $O<\begin{matrix}CHPh \\ | \\ CHMe\end{matrix}$, and then in rupture of the oxygen bridge in two ways, with formation of a mixture of isomeric amines; preliminary methylation of the hydroxyl group causes the reaction to proceed in one definite direction.

When the base obtained according to equation (4) is heated with hydrobromic acid saturated at 0°, the methoxy-group is hydrolysed, and perhaps part of the amino-alcohol thus formed converted into the bromo-amine. In any case, when the product of the reaction is evaporated and the residual mixture of hydrobromides is boiled with water, the bromine is replaced by hydroxyl and racemic ψ-ephedrine, obtained in 45% yield; the melting point of this base, 117—118°, is that of natural ψ-ephedrine, but the respective crystalline forms and other properties are different.

By repeated crystallisation of the *d*-tartrate, the racemic ψ-ephedrine may be separated into its *d*- and *l*-components. The former is identical with natural ψ-ephedrine, so that the Ladenburg-Schmidt constitution for this compound is confirmed.

l-ψ-Ephedrine, which does not occur naturally, has the same properties as the dextro-compound, except that its optical rotation is of opposite sign.

Schmidt (A., 1908, i, 452) showed that, when heated with hydrochloric acid, ephedrine and ψ-ephedrine undergo interconversion, and, by taking advantage of this observation, the author has obtained the two synthetic ephedrines from *d*- and *l*-ψ-ephedrines. Synthetic *l*-ephedrine hydrochloride has the same melting point and optical rotation as natural ephedrine hydrochloride, and the synthetic lævo-base the same melting point as the natural base. Synthetic *d*-ephedrine and its hydrochloride have the expected properties.

It is probable, but has not been definitely established, that in ψ-ephedrine the hydroxyl and methylamino-groups stand near to, and in ephedrine distant from, one another.

Schmidt and Calliess's statement (A., 1912, i, 644) that natural ψ-ephedrine may be converted readily into natural ephedrine by barium hydroxide at 170—180° is controverted.

αβ-Dibromo-α-methoxypropane, $C_4H_8OBr_2$, forms a water-clear liquid, b. p. 66—67°/13 mm. or 71—72°/16 mm., which emits an intensely lachrymatory vapour.

β-Bromo-α-methoxyphenylpropane, OMe·CHPh·CHMeBr, is obtained as a transparent liquid coloured brownish-violet by traces of iodine, b. p. 125—126°/18 mm.; its odour is peculiar and penetrating, but with the diluted liquid is not unpleasant.

α-Methoxy-β-methylaminophenylpropane,

OMe·CHPh·CHMe·NHMe,

forms a pale yellow oil with an aminic odour, b. p. 105—110°/13 mm., and its *aurichloride*, $C_{11}H_{17}ON,HAuCl_4$, shining, golden-yellow needles, m. p. 116·5—117·5° (clear at 121°).

Racemic *ψ-ephedrine*, $C_{10}H_{15}ON$, forms silky, felted needles, m. p. 118·2°, and its *hydrochloride*, $C_{10}H_{15}ON,HCl$, has m. p. 164°. The *aurichloride*, which forms crystals, m. p. 186—187°, has the abnormal composition $(C_{10}H_{15}ON)_2,HCl,HAuCl_4$, the racemic compound, $(C_{10}H_{15}ON)_2$, apparently playing the part of a base with two nitrogen atoms, at only one of which the gold chloride is taken up.

d-ψ-Ephedrine, obtained synthetically, has m. p. 118—118·7° and $[\alpha]_D^{22.5}$ in alcohol $+52·9°$; for natural ψ-ephedrine, Schmidt and Emde (A., 1906, i, 978) gave the rotation $+51·24°$, and Gadamer (A., 1909, i, 49) $+51·20°$. The synthetic hydrochloride has m. p. 182·5—183·5° and $[\alpha]_D^{20}$ $+62·8°$; for the natural hydrochloride, Miller (A., 1903, i, 110) gave m. p. 181—182°, and Flächer (A., 1904, i, 769) $[\alpha]_D^{20}$ $+62·05°$. The aurichlorides of the natural and synthetic bases have m. p. 126·5—127·5°. The synthetic phenylthiocarbamide has m. p. 120·5—121·5° and $[\alpha]_D^{20}$ $+23·4°$, the respective values for the natural derivative being 121—123° and $+22·8°$ (Gadamer, *loc. cit.*).

l-*ψ-Ephedrine* crystallises in white leaflets, m. p. 118—118·7°, $[\alpha]_D^{22.5}$ $-52·50°$. The *hydrochloride* crystallises in needles, m. p.

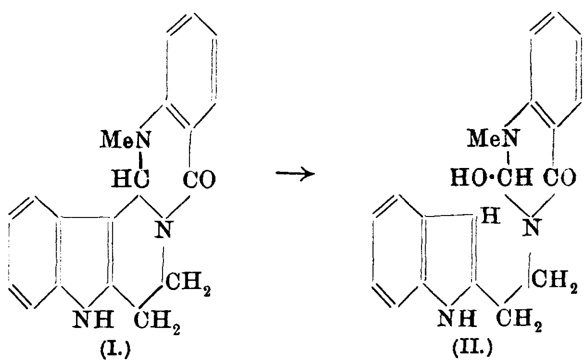
181·5—182·5°, $[\alpha]_D^{20}$ −62·1°, and the *aurichloride* forms crystals, m. p. 126·5—127·5°. The *phenylthiocarbamide* has m. p. 120—121° and $[\alpha]_D^{20}$ −23·1°.

Synthetic *l*-ephedrine, prepared by the action of hydrochloric acid on synthetic *d*-ψ-ephedrine, has m. p. 39—40°, the natural base having m. p. 39·5—40·5°. The hydrochloride has m. p. 217·3—217·8° and $[\alpha]_D^{20}$ −34·5°, the values for the natural salt being 216·8—217·3° and −35·3° (Gadamer, *loc. cit.*) or −34·9° (Schmidt and Emde, A., 1906, i, 978).

d-*Ephedrine*, prepared from *l*-ψ-ephedrine, has m. p. 39·5—40·5°, and its *hydrochloride*, m. p. 217·3—217·7° and $[\alpha]_D^{20}$ +35·8°.

r-*Ephedrine* has m. p. 73—74°, and its *hydrochloride*, m. p. 188·5—189·5°. T. H. P.

Evodiamine and Rutaecarpine. Y. Asahina and S. Mayeda (*J. Pharm. Soc. Japan*, 1916, No. 416. Compare A., 1916, i, 621).—The acetone extract of the fruit of *Evodia rutaecarpa* leaves, on evaporation, crystals and an oil; the latter is removed by methyl alcohol. The crystalline mixture (1·5% of the fruit) consists of two alkaloids and a little of the lactone, evodin (A., 1916, i, 238). The latter is hydrolysed by boiling alcoholic potassium hydroxide and removed. The alkaloids are separated by crystallisation from alcohol, evodiamine being the less soluble and the more abundant. The filtrate is boiled with 2% alcoholic hydrochloric acid until the evodiamine remaining in it is converted into "iso*evodiamine*" hydrochloride. This is more soluble in water than rutaecarpine hydrochloride, which is thus obtained pure on crystallisation. Evodiamine (I), $C_{19}H_{17}ON_3$,



(I.) (II.)

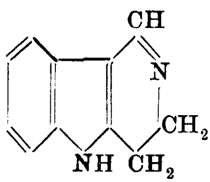
m. p. 278°, $[\alpha]_D^{15}$ +352° in acetone, is a weak base insoluble in dilute acids. On heating with alcoholic hydrochloric acid until it no longer gives with concentrated sulphuric acid the colour reaction of A., 1916, i, 621, but only a yellow colour, it is changed to "*iso*evodiamine" [evodiamine hydrate] (II), $C_{19}H_{19}O_2N_3$, m. p. 146—147°, optically inactive. This base forms a *hydrochloride*, crystallising in hexagonal or rhombic plates from alcohol, and in fine prisms

from water; the hydrated salt melts at 255—256°, the anhydrous at 265—267°. The *nitroso*-compound melts at 120°. Acetic anhydride at 150° changes *iso*evodiamine back to evodiamine, which is then, however, optically inactive. Free *iso*evodiamine gives the pinewood reaction, and is split by alcoholic potassium hydroxide into *N*-methylanthranilic acid, carbon dioxide, and a *base*, $C_{10}H_{12}N_2$, isomeric with 3-β-aminoethylindole (T., 1911, **99**, 270; obtained also by decarboxylation of tryptophan, A., 1911, ii, 1120). Both bases give an orange *picrate* melting at 242° and a *hydrochloride* melting at 246°; the free base from *iso*evodiamine melts at 120°, its N-*benzoyl* derivative at 173—174°. It is optically inactive, and cannot be resolved with tartaric acid. Fusion with potassium hydroxide yields 2-indolecarboxylic acid. The base is therefore considered to be 2-β-aminoethylindole. It is not very poisonous, and strongly raises the blood-pressure. The *benzylidene* compound,

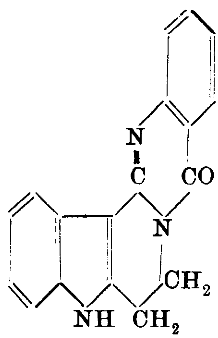
$$C_8H_6N\cdot CH_2\cdot CH_2\cdot N\colon CHPh,$$

melts at 122°, the *phthalyl* derivative at 165°, the *phenylcarbamido*-derivative at 181°, the *phenylthiocarbamido*-derivative at 158—159°, and the *quaternary iodide*, $C_{10}H_{10}N_2Me_3I$, at 194—196°.

Evodiamine is not attacked by aqueous alkali, but is split by boiling alcoholic potassium hydroxide into *N*-methylanthranilic acid and a base, $C_{11}H_{10}N_2$, regarded as 3:4-dihydro-5-carboline (III) (compare Perkin and Robinson, T., 1919, **115**, 970).



(III.)



(IV.)

Rutaecarpine (IV), $C_{18}H_{13}ON_3$, m. p. 258°, gives with concentrated sulphuric acid only a yellow colour. Phosphorus pentachloride does not form a substitution product, but only the yellow hydrochloride, readily dissociated by water. Methyl iodide and nitrous acid do not attack it, but nevertheless a *monoacetyl* derivative, m. p. 184—186°, and a *monobenzoyl* derivative, m. p. 194°, are obtained. The formation of these acyl derivatives is explained by reference to Heller's observation (A., 1904, i, 942) that phenyldihydroquinazoline gives a 1-benzoyl-2-benzoxy-derivative; rutaecarpine is considered to form a similarly constituted intermediate compound, which loses one molecule of acetic (or benzoic) acid, the resulting acyl compound being derived from *iso*carboline (the

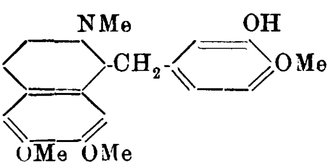
hydrogen is thus transferred from pyrrole-*N* to anthranilic acid-*N*). Rutaecarpine gives no pinewood reaction, and is not decomposed by potassium hydroxide in ethyl alcohol, but in boiling amyl alcohol there are formed anthranilic acid and a small quantity of a base, yielding a picrate, m. p. 150°. Fusion with potassium hydroxide yields indole-2-carboxylic acid.

The colour reaction of evodiamine with concentrated sulphuric acid is considered to be due to the formation of tri-indylmethane dyes, in which the methane carbon atom is the tertiary atom adjoining the 3-position of the indole group of one of three molecules (compare Ellinger and Flamand, A., 1911, i, 329; Freund and Lebach, A., 1905, i, 663). G. B.

Loturine. ERNST SPÄTH (*Monatsh.*, 1920, **41**, 401—403).—The physical and crystallographic characters of loturine (compare Hesse, A., 1879, 73) show that this alkaloid is identical with aribine and harman (compare Späth, A., 1920, i, 327). It is possible that colloturine, m. p. 234°, the second base found by Hesse in *Symplocos racemosa*, is loturine in another crystalline form.

T. H. P.

Constitution of Laudanine. ERNST SPÄTH (*Monatsh.*, 1920, **41**, 297—304).—Goldschmiedt (A., 1893, i, 181) has shown that laudanine yields metahemipinic acid on oxidation, so that the two hydroxyl groups of the *iso*quinoline are methylated, and the free hydroxyl group must be attached to the benzyl residue. The author finds that ethyl-laudanine, in which the phenolic hydroxyl group is protected and marked by an ethyl group, yields 4-methoxy-3-ethoxybenzoic acid (ethyl*iso*vanillic acid) on oxidation; similarly, ethylcarbonatolaudanine, in which the hydroxyl of laudanine is replaced by an ethyl-carbonato-group, gives ethylcarbonato*iso*vanillic acid. It follows from these results that the phenolic hydroxyl of laudanine occupies position 3 of the benzyl residue, and that laudanine possesses the annexed formula. All the formulæ previously proposed for laudanine (compare Decker and Eichler, A., 1913, i, 289; Hess and Weltzien, A., 1920, i, 328) are therefore inaccurate.



From laudanine and diazomethane, racemic laudanosine has been obtained, the connexion between these two alkaloids being thus confirmed (compare Hesse, A., 1902, i, 307).

Laudanine belongs to the small number of alkaloids which exhibit no optical activity, in spite of the presence of an asymmetric carbon atom. Whether the optical inactivity depends on the formation, during the synthesis of the base, of an intermediate product of the structure $>$–CH:C$<_{NMe-}$, which then yields laudanine by hydration or enzyme action (compare Hess, *loc. cit.*), or whether, like hyoscyamine, laudanine is readily racemisable, can

be decided only by experiments on the active base, as yet unknown.

4-*Methoxy*-3-*ethoxybenzoic acid* (*ethyl*iso*vanillic acid*), $C_{10}H_{12}O_4$, obtained by the action of permanganate on ethyl-laudanine in acid solution, or as ester by the action of sodium and ethyl iodide on ethyl *iso*vanillate, forms crystals, m. p. 166°; its *ethyl* ester has m. p. 62°. *Ethyl* iso*vanillate*, $OH{\cdot}C_6H_3(OMe){\cdot}CO_2Et$, forms crystals, m. p. 51—52°.

4-*Methoxy*-3-*ethylcarbonatobenzoic acid* (*ethylcarbonato*iso*vanillic acid*), $C_{11}H_{12}O_6$, prepared by oxidising ethylcarbonatolaudanine by means of permanganate or by the action of ethyl chlorocarbonate on *iso*vanillic acid, forms crystals, m. p. 186—187°. 3-*Methoxy*-4-*ethylcarbonatobenzoic acid*, prepared, for purposes of comparison, from vanillic acid, forms shining crystals, m. p. 149—150°.

The transformation of laudanine into laudanosine, as described by Hesse (*loc. cit.*), is confirmed. T. H. P.

Derivatives of γ-Aminovaleraldehyde. BURCKHARDT HELFERICH and WALTER DOMMER (*Ber.*, 1920, **53**, [*B*], 2004—2017).—It has been shown previously that γ-hydroxyaldehydes can exist in open and cyclic forms (A., 1919, i, 386; 1920, i, 11); it is now shown that this is also the case with γ-aminoaldehydes.

ζ-*Chloro*-β-*methyl*-Δ^β-*heptene*, $CHMeCl{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$, colourless, mobile liquid, b. p. 60—61°/15 mm., D_4^{18} 0·8931, n_D^{18} 1·4458, is prepared by the action of thionyl chloride on methylheptenol, and is transformed by ozone in glacial acetic acid solution into γ-*chlorovaleraldehyde*, colourless liquid, b. p. 70—71°/16 mm., D_4^{18} 1·0724, n_D^{18} 1·4476 (corresponding *dimethyl acetal*, b. p. 76°/13 mm., D_4^{18} 1·0116, n_D^{18} 1·4325). ζ-Chloro-β-methylheptene is converted by an alcoholic solution of dimethylamine at 180° into ζ-*dimethylamino*-β-*methyl*-Δ^β-*heptene*, colourless, mobile liquid, b. p. 69°/15 mm., D_4^{18} 0·7965, n_D^{18} 1·4440, from which, however, γ-dimethylaminovaleraldehyde could not be isolated in the pure condition. Attempts to prepare γ-aminovaleraldehyde from ζ-amino-β-methylheptene were similarly unsuccessful. ζ-*Formylamino*-β-*methyl*-Δ^β-*heptene* is a colourless, mobile oil, b. p. 143°/13 mm., D_4^{18} 0·92003, n_D^{1} 1·4669, which is converted by treatment with ozone into γ-*formylaminovaleraldehyde*, colourless liquid, b. p. 84°/14 mm., the yield, however, being very poor. Better results are obtained with ζ-*acetylamino*-β-*methyl*-Δ^β-*heptene*, colourless liquid, b. p. 150—151°/13 mm., D_4^{18} 0·9142, n_D^{18} 1·4651, which is similarly transformed into γ-*acetylaminovaleraldehyde*, $NHAc{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$ and $CHMe{<}{\substack{CH_2{\cdot}CH_2\\ NAc}}{>}CH{\cdot}OH$, colourless oil, b. p. 102—103°/15 mm., D_4^{18} 1·054, n_D^{18} 1·4695. ζ-*Propionylamino*-β-*methyl*-Δ^β-*heptene*, colourless liquid, b. p. 156°/14 mm., D_4^{18} 0·9084, n_D^{18} 1·4648, is converted by ozone in glacial acetic acid solution into 1-*propionyl*-5-*methyl*-Δ^2-*pyrroline*,

$$COEt{\cdot}N{<}{\substack{CHMe\\ CH{:}CH}}{>}CH_2,$$

b. p. 98—99°/12 mm., D_4^{18} 1·0013, n_D^{18} 1·4852. *ζ-Benzoylamino-β-methyl-Δ^β-heptene*, colourless crystals, m. p. 87—88°, is converted by ozone into a product, which, when distilled under diminished pressure, loses water and passes into 1-*benzoyl*-5-*methyl*-Δ²-*pyrroline*, pale yellow oil, b. p. 141—142°/4 mm., D_4^{18} 1·0974, n_D^{18} 1·5559.

The γ-acylaminovaleraldehydes reduce Fehling's solution distinctly, although without invariable precipitation of cuprous oxide. Their most remarkable property is their distinct acidity towards litmus, which, however, is not sufficiently marked to permit their titration with alkali hydroxide, even in the presence of phenolphthalein. This behaviour is scarcely reconcilable with the open-chain structure, but can readily be accounted for by the assumption of even a partial conversion into the *cyclo*-form. The most conclusive evidence of the existence of the cyclic structures is derived from the conversion of γ-acetylaminovaleraldehyde by methyl-alcoholic hydrogen chloride into the corresponding *semi-acetal* (1-*acetyl*-5-*methoxy*-2-*methylpyrrolidine*),

$$\begin{array}{l}CH_2\text{——}CH_2 \\ | \\ CHMe\cdot NAc\end{array}\!\!>\!CH\cdot OMe,$$

colourless liquid, b. p. 112°/13 mm., D_4^{17} 1·0276, n_D^{18} 1·4650; when similarly treated, γ-propionylaminovaleraldehyde gives 1-*propionyl*-5-*methoxy*-2-*methylpyrrolidine*, colourless oil, b. p. 122—123°/13 mm., D_4^{23} 1·0029, n_D^{23} 1·4599. H. W.

Manufacture of Pyridine Bases. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Brit. Pat. 146869).—Pyridine bases are obtained by heating paracetaldehyde with aqueous ammonia, working preferably under stoicheiometric conditions, and not raising the temperature above 200°. For example, 132 parts of paracetaldehyde, when heated with 255 parts of 5% aqueous ammonia in an autoclave for four hours at 140°, four hours at 160°, and finally four hours at 180°, give a mixture of pyridine bases consisting for the most part of 2-methyl-5-ethylpyridine, the yield amounting to about 68% of the theoretical. G. F. M.

Syntheses of 4-Piperidone. L. RUZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1920, **3**, 806—818).—Several derivatives of 4-piperidone with substituents in positions 2 and 6 are well known, such as nortropinone, triacetonamine, and vinyldiacetonamine, and it was expected that the unsubstituted piperidone would be likewise rather stable. This expectation was a hindrance in the attempts to synthesise the compound, for it really tends to form complex intermolecular condensation products most readily, and four methods were tried before the goal was reached.

In the first place, since 4-hydroxypyridine reacts as 4-pyridone, an attempt was made to reduce it by means of platinum and hydrogen to 4-piperidone, but the only product was 4-piperidol (compare Emmert, A., 1916, i, 667). As a second method, the re-

oxidation of this secondary alcohol by means of chromic acid was tried. Attempts to isolate the oxidation product after neutralisation were fruitless, but by adding benzaldehyde and saturating with hydrogen chloride, a derivative of the desired substance was isolated, namely, 3:5-*dibenzylidene*-4-*piperidone hydrochloride*, which forms pale yellow needles, m. p. 275—277° (decomp.). Attempts to substitute 1-benzoyl-4-piperidol in this oxidation also failed, for in the benzoylation of the piperidol it is the *O*-benzoate which is formed. This has b. p. 240°/12 mm. (Emmert and Dorn, A., 1915, i, 584, gave 170°/12 mm.).

A third method consisted in the substitution of formaldehyde for its homologues in Petrenko-Kritschenko's condensation with acetonedicarboxylates and ammonia (A., 1912, i, 128), but this gave no result.

The most successful process was the condensation of ethyl $\beta\beta'$-iminodipropionate by boiling with sodium in xylene. The intermediate ester was hydrolysed, and carbon dioxide expelled by boiling with hydrochloric acid, and ultimately 4-*piperidone* was isolated as a mobile oil with basic odour. The oil changes in a short time, especially when heated, into a solid, odourless *condensation product*, which yields no oxime or benzoyl derivative, but is reconverted into the simple compound by boiling with hydrochloric acid, since benzaldehyde produces from the solution the above 3:5-dibenzylidene-4-piperidone hydrochloride.

Ethyl $\beta\beta'$-*iminodipropionate*, $NH(CH_2\cdot CH_2\cdot CO_2Et)_2$, b. p. 112—114°/0·2 mm., is prepared by the condensation of ethyl β-iodopropionate with ethyl β-aminopropionate hydrochloride (Hale and Honan, A., 1919, i, 469) in the presence of sodium ethoxide, but a considerable quantity of "*ethyl* $\beta\beta'\beta''$-*nitrilotripropionate*," $N(CH_2\cdot CH_2\cdot CO_2Et)_3$, b. p. 158—160°/0·2 mm., is formed as well. The latter is scarcely soluble in water, but the former dissolves freely, and also yields a *benzoyl* derivative, b. p. 198°/0·2 mm.

Improvements in the preparation of ethyl acetonedioxalate and in the methylation of 4-pyridone (4-hydroxypyridine) are also described. J. C. W.

isoCyanine Dyes from 4-Methylquinoline and its Homologues. ELLIOT Q. ADAMS and HERBERT L. HALLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2389—2391).—The quaternary additive products of pure 4-methylquinoline (or its homologues), when treated with alcoholic alkalis in hot concentrated solution, give dyes of the *iso*cyanine type, similar to, but not identical with, those given by the corresponding derivatives of quinaldine. *iso*Cyanines of this type have been prepared from 4-methylquinoline methiodide and ethiodide, and from 4:6-dimethylquinoline methiodide, ethiodide, and methyl nitrate. This formation of *iso*cyanines from 4-methylquinoline confirms the hypothesis that these dyes contain two quinoline nuclei attached to a central carbon atom at positions 4 and 2', respectively. W. G.

The Preparation of 4-Methylquinoline and Related Bases. LOUIS A. MIKESKA (*J. Amer. Chem. Soc.*, 1920, **42**, 2396—2397).—A detailed account is given of the preparation of 4-methylquinoline from acetone, formaldehyde, and aniline. If the aniline is replaced by *p*-toluidine, 4:6-dimethylquinoline is obtained, and if *p*-phenetidine is used, 6-ethoxy-4-methylquinoline is obtained, giving an ethiodide, m. p. 187°. W. G.

Tetramethylquinolines. LOUIS A. MIKESKA and ELLIOT Q. ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 2394—2396).—For the preparation of the tetramethylquinolines, the xylidines were submitted to Skraup's synthesis. It cannot be applied to *m*-2-xylidine. *s*-Xylidine gave 2 : 4 : 5 : 7-*tetramethylquinoline*, m. p. 59°; *p*-xylidine gave 2:4:5:8-*tetramethylquinoline*, m. p. 131, and *m*-4-xylidine gave 2:4:6:8-tetramethylquinoline, m. p. 86°. . The last compound has previously been prepared by Levin and Riehm (A., 1886, 721), but wrongly called 2:4:5:6- or 2:4:6:7-tetramethylquinoline. W. G.

Synthesis of Photosensitising Dyes. II. Dicyanine "A." LOUIS A. MIKESKA, HERBERT L. HALLER, and ELLIOT Q. ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 2392—2394. Compare A., 1919, i, 416).—When *p*-phenetidine is condensed with paracetaldehyde and acetone, and the product heated with acetic anhydride, and finally diazotised, and the diazo-compound destroyed by heating the sclution on a water-bath, 6-*ethoxy*-2:4-*dimethylquinoline*, b. p. 314—316°, is obtained, which gives a *sulphate* and an *ethiodide*. If the latter is converted into the ethonitrate, and this is treated with sodium ethoxide in absolute alcohol, air being bubbled through the mixture, dicyanine "A" nitrate is obtained as grass-green crystals. If the ethiodide of 6-ethoxy-2:4-dimethylquinoline is treated directly with sodium methoxide in methyl alcohol, dicyanine "A" iodide is obtained. W. G.

The Methiodides of the Condensation Products of some Cyclic Aldehydes with Quinaldine and α-Picoline, and their possible value as Indicators in Acidimetry. LOUIS F. WERNER (*J. Amer. Chem. Soc.*, 1920, **42**, 2309—2314).—The methiodides of the condensation products of various cyclic aldehydes with quinaldine were prepared, and their behaviour with sodium hydroxide determined. The results show that, in order that the methiodides of compounds of this type may have the properties of an indicator, there must be a phenolic hydroxyl group attached to the nucleus of the aldehyde used in their preparation. In order that these methiodides, where suitable, may be used as indicators, the hydriodic acid first formed by their hydrolysis in water must be neutralised with alkali. The following compounds are described.

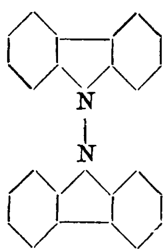
Furfuraldehyde when condensed with quinaldine yields 2-β-*furylvinylquinoline*, $C_4H_3O\cdot C_2H_2\cdot C_9H_6N$, m. p. 56° (corr.), giving a *hydrochloride* and a *methiodide*, m. p. 226·2° (corr.).

2-mp-*Methylenedioxystyrylpyridine methiodide*, $C_7H_5O_2{\cdot}C_2H_2{\cdot}C_6H_8NI$, has m. p. 276° (corr.); 2-*styrylquinoline methiodide*, $C_6H_5{\cdot}C_2H_2{\cdot}C_{10}H_9NI$, has m. p. 235·2° (corr.; decomp.); 2-o-*hydroxystyrylquinoline methiodide*, $C_6H_5O{\cdot}C_2H_2{\cdot}C_{10}H_9NI$, has m. p. 236° (corr.); 2-p-*hydroxystyrylquinoline methiodide* has m. p. 250·8° (corr.; decomp.); 2-p-*hydroxy*-m-*methoxystyrylquinoline methiodide*, $CH_3O{\cdot}C_6H_3(OH){\cdot}C_2H_2{\cdot}C_{10}H_9NI$, has m. p. 267° (corr.; decomp.); 2-mp-*dihydroxystyrylquinoline*, m. p. 244·6° (corr.), gives a *methiodide*, m. p. 266·8° (corr.; decomp.). W. G.

2 : 4-Dimethylquinoline, 4-Phenyl-2-methylquinoline, and 2 : 4 : 6-Trimethyl-quinoline. OTTO FISCHER, G. SCHEIBE, PAULA MERKEL, and R. MÜLLER (*J. pr. Chem.*, 1919, [ii], **100**, 91—105).—2 : 4-Dimethyl- and 2 : 4 : 6-trimethyl-quinolines are best prepared by the method of Combes (A., 1888, 504). In each case, the methyl group in the 2-position is much more reactive towards aldehydes than that in the 4-position. 2-*Styryl-4-methylquinoline*, $C_{18}H_{15}N$, prisms, m. p. 120—121°, forms a *hydrochloride*, $C_{18}H_{15}N,HCl,2H_2O$, m. p. 221—222°, and a *picrate*, $C_{24}H_{18}O_7N_4$, yellow needles, decomp. 233—239°. 2 : 4-*Distyrylquinoline*, $C_{25}H_{19}N$, m. p. 118°. 2-o-*Nitrobenzyloxymethyl*-4-*methylquinoline*, from *a*-nitrobenzaldehyde and dimethylquinoline, $C_{18}H_{16}O_3N_2$, needles, m. p. 138°; 2 : 4-*di*-o-*nitrostyrylquinoline*, $C_{25}H_{17}O_4N_3$, a yellow, crystalline powder, m. p. 230°. 4-*Phenyl*-2-*styrylquinoline*, $C_{23}H_{18}NCl$, needles, m. p. 114—115°; 4-*phenyl*-2-o-*nitrobenzyloxymethylquinoline*, $C_{23}H_{18}O_3N_2$, m. p. 136—137°; 4-*phenyl*-2-p-*nitrobenzyloxymethylquinoline*, $C_{23}H_{18}O_3N_2$, needles, m. p. 137°. The following salts of 2 : 4 : 6-trimethylquinoline were prepared: the *hydrobromide*, $C_{12}H_{14}NBr$, needles, decomp. 265—270°; the *aurichloride*, $C_{12}H_{14}NCl_4Au$, yellow needles, m. p. 140° (decomp.); the *picrolonate*, $C_{22}H_{21}O_5N_5$, yellow needles, m. p. 245°; the *ethochloride*, $C_{14}H_{18}NCl$, needles, decomp. 247°; the *ethobromide*, $C_{14}H_{18}NBr,H_2O$, leaflets, decomp. 246°. 2-*Styryl*-4 : 6-*dimethylquinoline*, $C_{19}H_{17}N$, needles, m. p. 106° (*hydrochloride*, $C_{19}H_{18}NCl$, decomp. 210°; *picrate*, $C_{25}H_{20}O_7N_4$, yellow needles, decomp. 223°). 2 : 4-*Distyryl*-6-m-*ethylquinoline*, $C_{26}H_{21}N$, m. p. 127°, gives a *picrate*, $C_{32}H_{24}O_7N_4$, decomp. 280°; a *picrolonate*, $C_{36}H_{29}O_5N_5$, yellow needles, decomp. 270°. 2-o-*Nitrobenzyloxymethyl*-4 : 6-*dimethylquinoline*, $C_{19}H_{18}ON_2$, needles, m. p. 154°; 2-o-*nitrostyryl*-4 : 6-*dimethylquinoline*, $C_{19}H_{16}O_2N_2$, yellow needles, m. p. 138°; 2-p-*nitrobenzyloxymethyl*-4 : 6-*dimethylquinoline*, $C_{19}H_{18}ON_2$, yellow needles, m. p. 132°; 2-p-*nitrostyryl*-4 : 6-*dimethylquinoline*, $C_{19}H_{16}O_2N_2$, yellow needles, m. p. 179°. 2 : 4 : 6-Trimethyltetrahydroquinoline, $C_{12}H_{17}N$, m. p. 80°, forms a *hydrochloride*, $C_{12}H_{18}NCl$, needles, m. p. 236—238°; a *picrate*, $C_{18}H_{20}O_7N_4$, yellow needles, m. p. 136°; a *picrolonate*, $C_{22}H_{25}O_5N_5$, m. p. 224°; an *acetyl* derivative, $C_{14}H_{18}ON$, needles, m. p. 74—75°; and a *nitrosoamine*, $C_{12}H_{16}ON_2$, yellow leaflets, m. p. *ca.* 50°.

The *condensation product* from benzoylacetone and *p*-toluidine, $C_{17}H_{17}ON$, yellow prisms, m. p. 92—93°, is converted by the process of Beyer (A., 1887, 849) into *4-phenyl-2:6-dimethylquinoline*, $C_{17}H_{15}N$, needles, m. p. 77—78°. J. K.

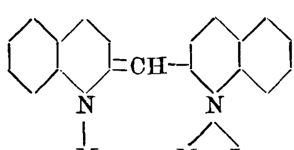
A Bivalent Nitrogen Derivative of Carbazole. GERALD E. K. BRANCH and JULIAN F. SMITH (*J. Amer. Chem. Soc.*, 1920, **42**, 2405—2413).—By the oxidation of carbazole with silver oxide in benzene solution two compounds are obtained, one soluble in ether and the other insoluble. The *compound* insoluble in ether has m. p. 283—287° (decomp.), and gives with dry nitric oxide a yellow, crystalline *compound*, m. p. above 270°. It is soluble in most organic solvents to a reddish-brown solution with a blue fluorescence. The molecular weight as determined in benzene by the cryoscopic method varies directly with the concentration, the substance being apparently very highly dissociated into odd molecules, in which the nitrogen is probably bivalent. It does not give a precipitate with oxygen in benzene solution, nor does it decolorise an iodine solution. In benzene solution it reacts violently with bromine to give a bromo-derivative of high m. p., and soluble in benzene.



From consideration of its chemical properties and molecular-weight determinations the compound would appear to be a di- or tri-carbazyl derivative of the substance the constitution of which is shown (annexed formula). W. G.

The Cyanine Dyes. III. The Constitution of Pinacyanol. WILLIAM HOBSON MILLS and FRANCES MARY HAMER (T., 1920, **117**, 1550—1562).

Quinocyanines. II. OTTO FISCHER and GÜNTHER SCHEIBE (*J. pr. Chem.*, 1919, [ii], **100**, 86—90).—The red dye obtained by treatment of the ψ-base from 4-phenyl-2-methylquinolyl methiodide in ethereal solution with air and carbon dioxide (A., 1919, i, 172) is also obtained by treating the ψ-base with 4-phenylquinolyl methiodide, and is therefore 4:4′-diphenyl-ψ-*iso*cyanine. 4:4′-Diphenyl-6:6′-dimethyl-ψ-*iso*cyanine, prepared from the ψ-base of 4-phenyl-2:6-dimethylquinolyl methiodide by means of air and carbon dioxide, gives a picrate, $C_{41}H_{33}O_7N_5$, which forms pointed pyramids with a green reflex, appearing red by transmitted light. The parent ψ-*iso*cyanine (annexed formula), prisms with a green reflex, obtained by addition of potassium hydroxide to a solution of 2-iodoquinolyl methiodide and 2-methylquinolyl methiodide in hydrochloric acid (compare Kaufmann, A., 1912, i, 502), was analysed in the form of its *picrate*. 2-Methyl*iso*cyanine forms a *benzylidene* derivative [*2-styryl*iso*cyanine*], $C_{31}H_{29}N_2I$, dark green



(I.)

crystals (*picrate*, $C_{37}H_{31}O_7N_5$, dark green prisms). 4:4′-*Distyryl-ψ-dicyanine* gives a *picrate*, $C_{48}H_{41}O_7N_5$, fine needles. The cyanines, ψ-*iso*cyanine, *iso*cyanine (ethyl red), pinacyanol (ψ-dicyanine), do not react with benzaldehyde. J. K.

Pyrimidines. LXXXIX. The Condensation of Benzamidine with Ethyl γ-Diethoxyacetoacetate. TREAT B. JOHNSON and LOUIS A. MIKESKA (*J. Amer. Chem. Soc.*, 1920, **42**, 2349—2355).—Benzamidine reacts with ethyl γ-diethoxyacetoacetate to form three different compounds according to the conditions of the reaction. If they are condensed together in aqueous solution in the presence of a molecular proportion of sodium hydroxide two products are obtained, namely, *γ-diethoxy-β-benzamidinocrotonylbenzamidine*, NH:CPh·NH·C[CH(OEt)$_2$]:CH·CO·NH·CPh:NH, m. p. 106°, which on further heating solidifies and then has a second m. p., 136°, and *6-oxy-2-phenyl-4-diethoxymethylpyrimidine* (annexed formula), m. p. 175°. This acetal, when digested with dilute hydrochloric acid, gives *6-oxy-4-aldehydo-2-phenylpyrimidine*, m. p. 205°, containing a molecule of water probably linked to the aldehyde group. It gives an *oxime*, m. p. 268° (decomp.), which when reduced by stannous chloride and hydrochloric acid yields *6-oxy-2-phenyl-4-aminomethylpyrimidine*, giving a *hydrochloride*, m. p. 263—265° (decomp.).

NH—CO
|　　|
CPh　CH
||　　||
N——C·CH(OEt)$_2$

When benzamidine and the β-ketonic ester are condensed in neutral solution the product is *γ-diethoxyacetoacetylbenzamidine*, NH:CPh·NH·CO·CH$_2$·CO·CH(OEt)$_2$, m. p. 145°, which, when heated above its melting point or treated with alkali, is converted into 6-oxy-2-phenyl-4-diethoxymethylpyrimidine. W. G.

Benzoyl Derivatives of Histidine and Histamine. OTTO GERNGROSS (*Zeitsch. physiol. Chem.*, 1919, **108**, 50—63).—Benzoyl derivatives of histidine and histamine were prepared by a general method of shaking the suspension of the iminazole derivative with benzoyl chloride. These compounds were found to be unstable. The following compounds were prepared: *exo*Benzoyl-*l*-histidine, $C_{13}H_{13}O_3N_3$, $[\alpha]_D^{20}$ −46·56°, m. p. 248° (corr.). *exo*Benzoyl-*l*-histidine methyl ester, $C_{14}H_{15}O_3N_3$, m. p. 160° (corr.). *eso-exo*Dibenzoyl-*l*-histidine methyl ester, $C_{21}H_{19}O_4N_3$, m. p. 108—109° (corr.). exo-*Benzoylhistamine*, $C_{12}H_{14}ON_3$, m. p. 148° (corr.). *eso-exo*Dibenzoylhistamine, $C_{19}H_{17}O_2N_3$. In the preparation of the last compound the hydrochloride of *exo*benzoylhistamine, $C_{12}H_{14}ON_3$,HCl, was also obtained. *eso-exo*Dibenzoylhistamine also yielded the monobenzoate of *exo*benzoylhistamine, $C_{19}H_{19}O_3N_3$, through the action of the atmosphere. The properties of the mono- and di-hydrochlorides and dinitrates of β-iminazolylethylamine are also described. S. S. Z.

Formation of Naphthiminazoles from 1-Nitroso-2-alkylnaphthylamines. OTTO FISCHER, CURT DIETRICH, and FRIEDRICH WEISS (*J. pr. Chem.*, 1920, [ii], **100**, 167—175).—1-Nitroso-2-methylnaphthylamine, from nitroso-β-naphthol and methylamine,

m. p. 148—149° (decomp.) (compare Morgan and Evens, T., 1919, **115**, 1126), gives a *hydrochloride*, $C_{11}H_{11}ON_2Cl$, yellow needles; a *hydrobromide*, scarlet needles; a *hydriodide*, yellowish-brown leaflets, a *picrate*, $C_{17}H_{13}O_8N_5$, yellow needles; an *acetyl* derivative, $C_{13}H_{12}O_2N_2$, yellow prisms, m. p. 140—141° (decomp.); and a *nitroso*-derivative, $C_{11}H_9O_2N_3$, a yellow powder. Alcoholic hydrochloric acid at 100°, or, better, zinc chloride and glacial acetic acid, convert the base into 1:2-naphthiminazole (compare Fischer and Hammerschmidt, A., 1916, i, 721). 1-Nitroso-2-acetylethylnaphthylamine, $C_{14}H_{14}O_2N_2$, forms yellow leaflets, decomp. 116—118°. 1-*Nitroso*-2-n-*propylnaphthylamine*, $C_{13}H_{14}ON_2$, light green prisms, m. p. 115° (decomp.) (*picrate*, yellow needles, decomp. 235°; *acetyl* derivative, $C_{15}H_{16}O_2N_2$, yellow leaflets, m. p. 114°), gives μ-*ethyl*-1:2-*naphthiminazole*, $C_{13}H_{12}N_2$, needles, m. p. 194°. 1-*Nitroso*-2-n-*butylnaphthylamine*, $C_{14}H_{16}ON_2$, dark green needles, m. p. 98—99° (*picrate*, yellow needles, decomp. 244°; *acetyl* derivative, $C_{16}H_{18}O_2N$, leaflets); μ-*propyl*-1:2-*naphthiminazole*, $C_{14}H_{14}N_2$, needles, m. p. 87°. 1-*Nitroso*-2-iso*amylnaphthylamine*, $C_{15}H_{18}ON_2$, leaflets, m. p. 82°, also gives a naphthiminazole. J. K.

Primary Quaternary Bases. S. Gabriel (*Ber.*, 1920, **53**, [*B*], 1985—1993).—The experiments were undertaken with the primary object of finding a convenient method for the preparation of vinylphthalimide (compare Bachstez, A., 1913, i, 1343), and for this purpose β-bromoethylphthalimide has been treated with pyridine and trimethylamine in the expectation that hydrogen bromide would thereby be eliminated. This, however, does not appear to be the case, the main products of the action being additive quaternary ammonium bromides, from which primary–quaternary bases are obtained by elimination of the phthalyl group.

β-Bromoethylphthalimide and pyridine, at the temperature of boiling water, readily yield β-*phthalimidoethylpyridinium bromide*, $C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}C_5NH_5Br$, leaflets or flat needles, m. p. about 235°, after softening at about 230° (the corresponding *dichromate*, orange-red needles, and *picrate*, long needles, m. p. 198°, are described); when an aqueous solution of the bromide is treated with moist silver oxide a transitory, marked alkalinity is observed, due to the formation of the ammonium base, which, however, is converted by hydrolysis and subsequent loss of water into the *substance*, $C_5NH_5{<}{\substack{C_2H_4{-}NH\\ O{\cdot}CO{\cdot}C_6H_4}}{>}CO$, colourless leaflets and needles, m. p. about 190° (decomp.), after softening from 140°. The latter is readily converted by hydrochloric acid into the *chloride*, $C_5NH_5Cl{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, hexagonal leaflets or short prisms ($+2H_2O$), m. p. (anhydrous) 180—181° after softening at 178°, and by picric and hydrobromic acids into the corresponding *picrate*, m. p. 159—160° (decomp.) after softening at 153°, and *bromide*, needles ($+2H_2O$), m. p. 65° after softening at 60°. Attempts to convert the betaine-like substance into the correspond-

ing ester by the use of a solution of methyl bromide in methyl alcohol were not completely successful, since the substance, although primarily formed, readily loses methyl bromide and passes into phthalimidoethylpyridinium bromide; similarly, methyl iodide gives *β-phthalimidoethylpyridinium iodide*, four-sided leaflets, m. p. about 239—240° (decomp.). *β-Phthalimidoethylpyridinium chloride*, rhombic crystals, m. p. 222—223°, is prepared by heating the anhydrous hydrochloride, $C_{15}H_{15}O_3N_2Cl$ (see above), in a vacuum at 210° or from chloroethylphthalimide and pyridine at 170°. The bromide, $C_{15}H_{13}O_2N_2Br$, is readily converted by aqueous sodium hydroxide into the *sodium* salt, $C_{15}H_{14}O_3N_2BrNa,2H_2O$, short prisms or rhombic plates.

The betaine-like substance is readily hydrolysed by boiling 20% hydrochloric acid to phthalic acid and *β-aminoethylpyridinium chloride hydrochloride*, $C_5NH_5Cl\cdot C_2H_4\cdot NH_2,HCl$, four- or six-sided plates, m. p. 208—210°. The latter yields a strongly alkaline solution when treated with moist silver oxide, but attempts to isolate the base in substance were unsuccessful. The *platinichloride* forms orange-yellow needles, m. p. about 264° (decomp.). The *bromide–hydrobromide*, long needles or rhombs, m. p. 206—208° after softening at 195°, and the *picrate*, $C_7H_{10}N_2,2C_6H_3O_7N_3$, crystalline powder, m. p. about 225—226° (decomp.), after softening at 215°, are described. The free β-aminoethylpyridinium base appears to have the constitution $C_5NH_5<\begin{matrix}C_6H_4\\|\\NH\end{matrix}$ and thus to be analogous to pyridinecholine, since, when treated with barium nitrite and hydrochloric acid and subsequently with sodium picrate, it yields a picrate identical with that prepared from the latter base. Reduction of the β-aminoethylpyridinium salts by tin and hydrochloric acid leads to the formation of β-aminoethylpiperidine.

β-Bromoethylphthalimide is converted by alcoholic trimethylamine solution at 100° into *trimethyl-β-phthalimidoethylammonium bromide*, $NMe_3Br\cdot C_2H_4\cdot C_8H_4O_2N$, colourless leaflets, m. p. 262—263°; similarly, iodoethylphthalimide gives *trimethyl-β-phthalimidoethylammonium iodide*, silvery crystals, m. p. 276° (decomp.) after softening. The corresponding *picrate*, long needles, m. p. 186—187°, *chloride*, leaflets, m. p. about 270° (decomp.) after softening at about 250°, and *aurichloride*, yellow, microcrystalline powder, are described. The chloride or bromide yields an alkaline solution when treated with silver oxide, which, however, becomes neutral when concentrated, and finally yields the *substance*, $NH<\begin{matrix}CO\cdot C_6H_4\cdot CO\\C_2H_4-NMe_3\end{matrix}>O$, silky needles, m. p. 258—259°, which yields a *picrate*, $C_{13}H_{18}O_3N_2,C_6H_3O_7N_3,H_2O$, m. p. 144° after softening at about 103°, and is converted by aqueous hydriodic acid into the *iodide*, $NMe_3I\cdot C_2H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, colourless rhombs, m. p. about 230° (decomp.). The chloride, $C_{13}H_{17}O_2N_2Cl$, is hydrolysed by boiling hydrochloric acid to phthalic acid and *trimethyl-β-aminoethylammonium chloride hydrochloride*,

$$NMe_3Cl\cdot C_2H_4\cdot NH_2,HCl,$$

rhombohedra, m. p. 254° (decomp.); the corresponding *platinichloride*, orange-yellow leaflets, m. p. about 245° (decomp.), and *picrate*, needles, m. p. 212—214° (decomp.), were analysed.

H. W.

Primary Quaternary Bases. MARGARETHE BOESE (*Ber.*, 1920, **53**, [*B*], 1994—1999).—γ-Bromopropylphthalimide reacts with pyridine in the same manner as the β-bromoethyl compound (preceding abstract); β-bromopropylphthalimide, on the other hand, is partly converted into an additive compound and partly into propenylphthalimide.

γ-*Phthalimidopropylpyridinium bromide*,

$$C_8H_4O_2{:}N{\cdot}[CH_2]_3{\cdot}C_5NH_5Br,$$

has m. p. 218° (decomp.) after softening at 214°; the corresponding *picrate* forms needles, m. p. 168° after softening at 166°, whilst the *dichromate* crystallises in deep yellow plates, which decompose above 200°. The corresponding betaine-like *compound*,

$$C_5NH_5{<}\begin{matrix}C_3H_6{\cdot}NH{\cdot}CO\\O{-}{-}{-}{-}{-}{-}{-}CO\end{matrix}{>}C_6H_4,H_2O,$$

forms slender needles, m. p. 86° (decomp.), and yields a *picrate*, $C_6H_2(NO_2)_3{\cdot}O{\cdot}C_5NH_5{\cdot}C_3H_6{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, yellow, rectangular plates, m. p. 139° after softening at 135°. Hydrolysis of phthalimidopropylpyridinium bromide with hydrobromic acid leads to the formation of γ-*aminopropylpyridinium bromide hydrobromide*, $C_5NH_5Br{\cdot}[CH_2]_3{\cdot}NH_2,HBr$, colourless, shining prisms, m. p. 176·5—177·5° (the corresponding *picrate* forms yellow, rhombic leaflets, m. p. 206° after darkening at about 200°).

β-Bromopropylphthalimide reacts less readily than the γ-compound with pyridine, but is converted by it at 162° into a mixture of propenylphthalimide, m. p. 151°, and β-*phthalimido*iso*propylpyridinium bromide*, $C_5NH_5Br{\cdot}CHMe{\cdot}CH_2{\cdot}N{:}C_8H_4O_2$, m. p. 225° after becoming discoloured at 210°; the corresponding *picrate* forms long, yellow needles, m. p. 190—191°, whilst the *dichromate* crystallises in orange-yellow rhombohedra or prisms, m. p. 196° (decomp.). Silver oxide converts the bromide into the betaine-like *derivative*, $C_5NH_5{<}\begin{matrix}C_3H_6{-}NH\\O{\cdot}CO{\cdot}C_6H_4\end{matrix}{>}CO$, colourless needles, m. p. 185° (decomp.) after softening and becoming discoloured at 160°, which is converted by the requisite acid into the *picrate*, yellow plates or needles, m. p. 149—150° (decomp.) after softening at 146°, *bromide*, colourless crystals, and *chloride*, rectangular plates, m. p. below 100°. Hydrobromic acid converts β-phthalimido*iso*propylpyridinium bromide into *amino*iso*propylpyridinium bromide hydrobromide*, $C_5NH_5Br{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2,HBr$, rhombs, m. p. 233—234° after softening at 227°; the corresponding *picrate* forms shining, yellow crystals, m. p. 197° after darkening at 190°, whilst the *platinichloride* crystallises in orange-yellow needles.

Propenylphthalimide (compare Johnston and Jones, A., 1911, i, 455) has been further investigated. It is converted by aqueous-alcoholic potassium hydroxide solution into *N*-propenylphthalamic

acid, needles, m. p. 136° (Johnston and Jones give m. p. 152°, due, apparently, to slow heating, and consequent conversion of the acid into propenylphthalimide); the *silver* salt is described. The acid is hydrolysed by boiling water to phthalic acid, ammonia, and propaldehyde, the unsaturated amine appearing to react with water in accordance with the scheme: $CHMe{:}CH{\cdot}NH_2 \xrightarrow{+H_2O} CHMe{:}CH{\cdot}OH \longrightarrow CHMe{\cdot}CHO$. Propenylphthalimide unites with chlorine in the presence of chloroform, yielding *α-phthalimido-αβ-dichloropropane*, $C_8H_4O_2{:}N{\cdot}CHCl{\cdot}CHMeCl$, colourless needles, m. p. 96°, which is converted by boiling water into phthalimide and acetol. N-*α-Bromopropylphthalimide*,

$$C_8H_4O_2{:}N{\cdot}CHEtBr,$$

colourless crystals, m. p. 89—90°, is prepared by the action of saturated hydrobromic acid solution at 0° on propenylphthalimide.

H. W.

Action of Ammonia and Amines on the Substituted Carbamides and Urethanes. II. Allophanic Ester. F. B. Dains and E. Wertheim (*J. Amer. Chem. Soc.*, 1920, **42**, 2303—2309. Compare A., 1919, i, 400).—If a primary arylamine reacts with allophanic ester, the product may be an arylallophanic ester or an arylbiuret:

$$RNH_2 + NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2Et = RNH{\cdot}CO{\cdot}NH{\cdot}CO_2Et + NH_3,$$
$$RNH_2 + NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2Et = RNH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + EtOH,$$

or, at higher temperatures, mono- and di-substituted carbamides are produced.

Ethyl allophanate and aniline heated in equimolecular proportions at 120—125° for one hour gave ethyl phenylallophanate, but if the proportion of aniline is doubled, the product is diphenylbiuret. At 160—170°, the products are phenylcarbamide and diphenylcarbamide. With *o*-anisidine at 130—140°, ethyl allophanate gives ethyl *o*-anisylallophanate, m. p. 125°, and *di-*o*-anisylbiuret*, m. p. 211—212°, but at 175° the product was di-*o*-anisylcarbamide. With *o*-toluidine, the products were ethyl *o*-tolylallophanate, *di-o-tolylbiuret*, m. p. 204—205°, o-*tolylcarbamide*, m. p. 189°, and *di-o-tolylcarbamide*, m. p. 245—247°, according to the conditions. Other condensation products which have been similarly prepared are m-*tolylcarbamide*, m. p. 143°; *di-*m-*tolylcarbamide*, m. p. 217°; *di-*m-*tolylbiuret*, m. p. 179°; ethyl *m*-nitrophenylallophanate; *di-*m-*nitrophenylbiuret*, m. p. 215—216°; m-*nitrophenylcarbamide*, m. p. 165°; *di-*m-*nitrophenylcarbamide*, m. p. 133—134°; *di-*p-*bromophenylbiuret*, m. p. 280° (decomp.); p-*bromophenylcarbamide*, m. p. 270° (decomp.); and *di-*p-*bromophenylcarbamide*.

Similar compounds were prepared from methyl allophanate, the methoxy-group, however, showing less stability towards the amine than the ethoxy-group. α-Phenylbiuret, m. p. 155°; diphenylbiuret and diphenylcarbamide were obtained from aniline and the methyl ester, but methyl phenylallophanate could not be obtained. With aniline, ethyl benzoylallophanate gave benzoylphenylcarbamide.

When heated together at 140°, phenylhydrazine and ethyl allophanate yielded *ethyl* 1-*phenylsemicarbazide*-4-*carboxylate*,

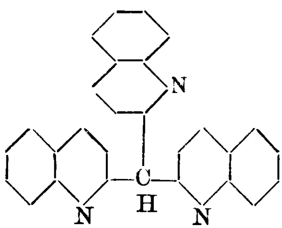
$NHPh\cdot NH\cdot CO\cdot NH\cdot CO_2Et$,

m. p. 175—176°, which, when heated above its melting point, gave 1-phenylurazole. With methyl allophanate, the intermediate semicarbazide could not be isolated, the only product being 1-phenylurazole. W. G.

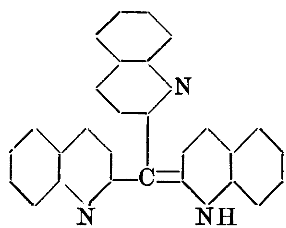
Carbazole-blue and Carbazole-violet. MAURICE COPISAROW (T., 1920, **117**, 1542—1550).

Di- and Tri-quinonylmethanes United by the Pyridine Nuclei. I. Tri-2-quinonylmethane. GÜNTER SCHEIBE and ERNST ROSSNER (*Ber.*, 1920, **53**, [*B*], 2064—2069).—Methyl- and halogen-substituted quinolines readily evolve hydrogen chloride when heated together, yielding quinonylmethanes, in which the methylene or methine carbon atom is united to the pyridine nucleus. The reaction appears to be general, and can, but with somewhat greater difficulty, be extended to the pyridine series.

Tri-2-*quinolylmethane* (formula I) is formed in 70% yield when



(I.)



(II.)

a mixture of 2-chloroquinoline (2 molecules) and 2-methylquinoline (1 molecule) is heated to its boiling point. It forms slender, pale red needles, which become colourless when preserved, and have m. p. about 199—200° after becoming red at 160° (*dihydrochloride*, green prisms, decomp. about 300°; *picrate*, $C_{40}H_{25}O_{14}N_9$, brownish-red prisms with green lustre, decomp. 212°; *perchlorate*, decomp. 242°). The colourless crystals yield a colourless solution in alcohol, which rapidly becomes yellowish-red when warmed, but re-forms the colourless needles when evaporated. The coloured solution shows two absorption bands at about 523 and 487 $\mu\mu$, which are observed with greater intensity in acid solution. If this solution is covered with ether and saturated with alkali, the red *base* (formula II) is precipitated in leaflets, which pass into the colourless modification when recrystallised. Attempts to prove the presence of the imino-group in the red base were not completely successful; when treated with an excess of methyl iodide at 100°, it gives a *compound*, $C_{29}H_{22}N_3I$, dark red prisms, m. p. about 245°, which loses methyl iodide when heated and regenerates the base on addition of alkali. With methyl iodide and alcohol at 100°, the *substance*, $C_{31}H_{28}N_3I_3$, coarse, brown crystals, m. p.

about 300°, is produced. Acetylation of the imino-hydrogen atom in the usual manner is not possible. Nitrous acid gives an unstable *product*, $C_{28}H_{18}O_2N_4$, colourless needles, decomp. 192°, which is also obtained by the action of nitric acid on an aqueous-alcoholic suspension of triquinonylmethane, and possibly contains the nitro-group united to the methane carbon atom.

Triquinonylmethane is oxidised by hydrogen peroxide to *triquinonylcarbinol*, colourless needles, m. p. 168°, which gives a *picrate*, $C_{34}H_{22}O_8N_6$, but could not be caused to yield a methiodide.

H. W.

The Preparation of Optically Active Hydrazines. I. The Preparation of *dl-p-αβ* Dimethylpropylphenylhydrazine. The Isolation of Pure *d-p-αβ*-Dimethylpropylaniline. J. W. E. Glattfeld and C. H. Milligan (*J. Amer. Chem. Soc.*, 1920, **42**, 2322—2328).—With a view to their use in the resolution of *dl*-hydroxy-acids, such as the C_4-saccharinic acids (this vol., i, 7), an attempt was made to prepare optically active phenylhydrazines. By the action of acetophenone on magnesium *iso*propyl iodide, *β-phenyl-γ-methyl-Δ^{β}-butene*, b. p. 187—188°, was obtained, which, on hydrogenation, yielded *αβ-dimethylpropylbenzene*, b. p. 186—188°. This hydrocarbon, on nitration in acetic acid solution, yielded p-*nitro-αβ-dimethylpropylbenzene*, b. p. 152—154°/20 mm., which, when reduced with tin and hydrochloric acid, yielded p-*αβ-dimethylpropylaniline*, $NH_2\cdot C_6H_4\cdot CHMe\cdot CHMe_2$, b. p. 129—131°/18 mm. This amine, when diazotised and the product reduced with zinc and acetic acid, gave dl-p-*αβ-dimethylpropylphenylhydrazine*, m. p. 60°, b. p. 147—150°/9 mm., giving a *hydrochloride*. This hydrazine was very unstable in air, and all attempts to resolve it into its optically active components were unsuccessful.

dl-p-αβ-Dimethylpropylaniline, as obtained above, was resolved into its optically active components by means of *d*-hydroxymethylenecamphor (compare Pope and Read, T., 1909, **95**, 171). The d-*aniline*, b. p. 139—140°/24 mm., had $[\alpha]_D + 0{\cdot}96°$; its *hydrochloride* had $[\alpha]_D + 0{\cdot}974°$, and its d-*hydroxymethylenecamphor* derivative had $[\alpha]_D + 300°$. The l-*aniline*, b. p. 139—140°/24 mm., had $[\alpha]_D + 0{\cdot}76°$; its *hydrochloride* had $[\alpha]_D^{20} + 0{\cdot}565°$, and its d-*hydroxymethylenecamphor* derivative had $[\alpha]_D^{20} + 229°$. W. G.

Certain Salts with *para-*, *ortho-*, and *meta*-Quinonoid Structure. II. R. Ciusa (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 146—150. Compare A., 1920, i, 256).—Benzoylformaldehyde-*p*-nitrophenylhydrazone, obtained by heating benzoylglyoxylic acid-*p*-nitrophenylhydrazone at its melting point, gives, when treated in xylene solution with alcoholic potassium hydroxide, the *compound*, $C_{22}H_{15}O_4N_5K_2$, which forms blue crystals with a golden reflection. Treatment of this potassium derivative with dilute sulphuric acid yields the *compound*,

$$NO_2\cdot C_6H_4\cdot NH\cdot N\colon CBz\cdot CBz\colon N\cdot NH_2,$$

which crystallises in golden-yellow, shining plates, m. p. 199°.

Benzoylformaldehyde-*o*-nitrophenylhydrazone also yields a similar *potassium* salt, $C_{22}H_{15}O_4N_5K_2$, crystallising in blue plates with a golden-yellow reflection.

As was shown by Angeli, ortho- and para-substituted compounds of the type $R\cdot C_6H_4\cdot R$ behave similarly to those of the form $R\cdot R$, since they react as if the benzene nucleus were non-existent. The formation of the compound, $C_{22}H_{17}O_4N_5$, may result from the decomposition of one molecule of benzoylformaldehyde-*p*-nitrophenylhydrazone, similarly to the decomposition of nitrohydroxylaminic acid, $CHBz{:}N\cdot N{:}C_6H_4{:}NO_2K \longrightarrow CHBz{:}N\cdot N{:} + C_6H_5\cdot NO_2$, and subsequent union of the residue, $CHBz{:}N\cdot N{:}$, with a second molecule of the nitrophenylhydrazone.

Hydrolysis of the potassium derivative of benzaldehyde-*p*-nitrophenylhydrazone (*loc. cit.*) by means of dilute sulphuric acid yields the original nitrophenylhydrazone itself, and the same occurs with the *potassium* compound of dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone, $C_{15}H_{15}O_2N_4K$, which forms violet scales with metallic reflection.

The *sodium* salt of benzaldehyde-*p*-nitrophenylhydrazone forms a violet powder; the rubidium, lithium, and calcium salts exist in solution, but readily undergo hydrolysis, and are difficult to obtain pure.

Since, on addition of alcoholic potassium hydroxide to the three nitrobenzaldehydephenylhydrazones in acetone solution, an intense green coloration appears, it is assumed that salt-formation occurs, with formation of a quinono-nitronic acid, at the expense of the aldehydic hydrogen atom:

$$NO_2\cdot C_6H_4\cdot CH{:}N\cdot NHPh \longrightarrow NO_2H{:}C_6H_4{:}C{:}N\cdot NHPh.$$

Such salts are of interest, as they contain the grouping $:C{:}C{:}N\cdot NK_2$, analogous to that of the hydrazenes, and are, indeed, related to the hydrazenes in the same way as the quinoketens are to the ketens. The alkali salts of these hydrazones appear to exist only in solution, but from *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone, mono- and di-potassium salts have been prepared; both the *monopotassium* salt, $NO_2\cdot C_6H_4\cdot CH{:}N\cdot N{:}C_6H_4\cdot NO_2K$, and the *dipotassium* salt, $KNO_2{:}C_6H_4{:}C{:}N\cdot N{:}C_6H_4\cdot NO_2K$, form brown, crystalline powders. T. H. P.

The Estimation of Tryptophan in Protein Material. PIERRE THOMAS (*Ann. Inst. Pasteur*, 1920, **34**, 701—708).—The author employs the colour test with *p*-dimethylaminobenzaldehyde for the estimation of tryptophan in the fully-digested protein. By this method, 1·7 to 1·8% of tryptophan was found in caseinogen, an amount which is in agreement with the results of Hopkins and Cole. J. C. D.

Colorimetric Investigation of Tryptophan. III. The Cleavage of Tryptophan during Hydrolysis of Proteins. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Zeitsch.*, 1920, **109**, 153—164).—The relative amounts of free and combined tryptophan were followed up by Voisenet's method during the hydrolysis

of protein by estimating this amino-acid in the fraction precipitated with phosphotungstic acid and in the residue. In the case of the hydrolysis of fibrin by tryptic digestion, only two-thirds of the total tryptophan was obtained in the free form. The authors do not think that tryptophan is in an "exposed position," as is alleged to be the case with tyrosine. S. S. Z.

The Humin Formed by the Acid Hydrolysis of Proteins. VI. The Effect of Acid Hydrolysis on Tryptophan. GEORGE E. HOLM and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1920, **42**, 2378—2385. Compare A., 1915, i, 726; 1916, i, 681; 1918, i, 84; 1920, i, 400, 450).—A study of the changes produced by boiling tryptophan with 20% hydrochloric acid for lengths of time varying from 12 to 144 hours. By prolonged acid hydrolysis, tryptophan is slowly altered, and parts of the molecule are broken down. In the absence of aldehydes or other reactive compounds, tryptophan only contributes an insignificant fraction of its nitrogen to the "acid-insoluble" humin. After 144 hours' boiling with acid, a much larger amount of the tryptophan appears in the "soluble humin," but as a normal protein hydrolysis rarely requires more than 24 hours' boiling, it appears extremely improbable that the "total" humin of such a hydrolysate is derived from tryptophan without the intervention of some other reactive compound. Tryptophan is relatively easily deaminised by boiling with 20% hydrochloric acid, and it is probable that some of the ammonia of a normal protein hydrolysate is derived from tryptophan, instead of being entirely derived from amide groupings. W. G.

The Methylation of Proteins. J. HERZIG (*Zeitsch. physiol. Chem.*, 1920, **111**, 223—227).—Some theoretical observations in connexion with the methylation of proteins, in view of the results obtained by Edlbacher (A., 1920, i, 896) and by Herzig (A., 1920, i, 896). S. S. Z.

Protein Reactions. II. The Action of Electrolytes on Serum Albumin. A. VON SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1920, **110**, 119—127).—Univalent cations of the highest discharge potential do not precipitate or change the charge of denaturated albumin. Bivalent cations of high discharge potential have only the capacity of changing the charge, whilst cations of a small discharge potential possess both properties. In the case of native albumin, which otherwise behaves like the denaturated protein in this respect, the change in the charge coincides with the maximum flocculation. S. S. Z.

Some Amino-acids from the Globulin of the Coconut as Determined by the Butyl Alcohol Extraction Method of Dakin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1920, **44**, 283—290).—Attention was confined chiefly to the

amino-acids remaining in the aqueous solution after the extraction. The following values were found: glutamic acid, 19·07%; aspartic acid, 5·12%; alanine, 2·67%; and serine, 1·76%. No hydroxyglutamic acid or glycine could be detected. From the amino-acids extracted by the butyl alcohol, 5·54% of proline and 0·64% of leucylvaline anhydride were isolated. It has not been ascertained whether the latter product is present in the protein molecule or is formed during extraction. J. C. D.

Hydrolysis of the Globulin of the Coconut, *Cocos nucifera*. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1920, **44**, 291—301).—By employing recent improvements in methods of protein hydrolysis, the authors have succeeded in accounting for 78·15% of the molecule of the globulin of the coconut. J. C. D.

Yeast-nucleic Acid. H. STEUDEL and E. PEISER (*Zeitsch. physiol. Chem.*, 1919, **108**, 42—49).—A sample of commercial yeast-nucleic acid with a ratio of P:N=1:1·77 was fractionated with lead acetate, sodium carbonate, and barium acetate into five fractions. With varying P:N ratios, as the reactions employed in the fractionation were not drastic enough to break up the nucleic acid molecule, the authors conclude that the substance was a mixture of several compounds. One of these fractions, with the ratio of P:N=1:2·09, on analysis gave the formula of the barium salt of yeast-nucleic acid, $(C_{29}H_{39}O_{23}N_{13}P_3)_2Ba_3$. S. S. Z.

Amino-acids of Gelatin. H. D. DAKIN (*J. Biol. Chem.*, 1920, **44**, 499—529. Compare A., 1919, i, 150).—An analysis of the product of hydrolysis of gelatin has been made, making use of the butyl alcohol method for the separation of certain groups of amino-acids.

The extraction of proline is best accomplished with butyl alcohol under reduced pressure, thus limiting secondary changes. Propyl alcohol may be used to complete the extraction of the hydroxyproline. The separation and isolation of proline and hydroxyproline are fully considered, and evidence is presented to show that gelatin may yield as much as 14% of the latter amino-acid. Hydroxyglutamic acid, valine, and *iso*leucine are absent from gelatin.

A new tricyclic peptide was isolated, which appears to be γ-*hydroxyprolylproline anhydride*,

$$\mathrm{OH\cdot CH}\left<\begin{array}{l}\mathrm{CH_2\cdot N{-}{-}CO\cdot CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH\cdot CO\cdot N{-}{-}CH_2}\end{array}\right>\mathrm{CH_2};$$

$[\alpha]_D^{20}$ $-142·0°$, m. p. 102—103° (from ether), 135—140° (from water). The cause of this variation in m. p. has not been determined. The preparation of the hydantoin derivatives of *l*-hydroxyproline and *r*-proline are described.

1-γ-*Hydroxyprolylhydantoin*, $\mathrm{OH\cdot CH}\left<\begin{array}{l}\mathrm{CH_2\cdot CH\cdot CO}\\ \mathrm{CH_2\cdot N{-}{-}CO}\end{array}\right>\mathrm{NH}$, forms needles, m. p. 162—165°, $[\alpha]_D^{20}$ $-7·2°$.

i-*Prolylhydantoin*, $CH_2<\begin{matrix}CH_2\cdot CH\cdot CO\\ \quad\; | \\ CH_2\cdot N—CO\end{matrix}>NH$, m. p. 142—143°, crystallises in highly refractive, hexagonal prisms.

The quantitative results of the amino-acid estimations on gelatin now show that 91·31% of the molecule has been accounted for. Unidentified sulphur compounds are present. J. C. D.

Theory of the Tanning (Hardening) Process in Dilute Gelatin Gels with Formaldehyde. L. Reiner (*Kolloid Zeitsch.*, 1920, **27**, 195—197).—The tanning (hardening) of gelatin gels by formaldehyde has been followed by observations on the softening, melting, and setting temperatures. It is shown that 2—3% solutions of formaldehyde tan (harden) 5% gelatin solutions in two or three minutes, whilst a 1% solution of formaldehyde requires several days. Hardened gelatin loses its power of melting, but the mass still softens at elevated temperatures; the softening temperature is dependent on the amount of hardening and the concentration of the gelatin. Hardened gelatin softens at temperatures higher than the melting point of the untreated material. The softening of the hardened gelatin commences at the centre of the mass and spreads through the mass, and, on raising the temperature sufficiently, the gelatin becomes liquid. If the softening temperature lies above 90°, then complete liquefaction is no longer possible. The hardening appears to occur more completely on the surface than in the interior of the mass. On cooling a melted, hardened gelatin, the solidifying point lies below that of the untreated gelatin. The above facts are explained as follows: formaldehyde does not attack gelatin uniformly; one part is hardened, whilst another remains unattacked. The hardened part forms a more or less coherent structure, and on continued action becomes much more coherent and encloses the unhardened portion of the solution. In this way, the gel loses its characteristic melting point, but if the structure is disturbed by melting, then the mass solidifies at the point of solidification of the unhardened gel. The relationship between the hardened and unhardened gelatin depends on the concentration of the aldehyde and the gelatin. The hardening process is shown to be reversible. If a hardened gel is digested at 100° with a little water, formaldehyde is evolved, and the gelatin is regained with its original physical properties. The hardening process may be entirely stopped and reversed by the addition of small quantities of ammonia. Consequently, by using the calculated quantities of ammonia, the hardening may be stopped at any point. Hypotheses to explain this action are put forward. J. F. S.

Comparison of the Chemical Constitution of Tussur Silks. Ryûgo Inouye, Suehiko Iwaoka, and Masaru Hirasawa (*J. Tokyo Chem. Soc.*, 1920, **41**, 876—898).—The silk layers of tussur cocoons from Ariake, in Japan (I), and Chi-kuan-shan, in Manchuria (II), were hydrolysed with hydrochloric acid, with the following results (figures in parenthesis show the percentages in

I and II): glycine (12·38, 16·80), alanine (15·27, 11·87), leucine (0·27, 0·25), aspartic acid (2·37, 4·08), glutamic acid (trace, trace), serine (0·55, 0·47), proline (0·26, 0·23), hydroxyproline (—, 0·18), phenylalanine (0·37, 1·18), and tyrosine (6·62, 3·86). In the original, these figures are compared with those of Japanese, Indian, and Chinese cocoons. K. K.

The Quantitative Action of Enzymes. G. TAMMANN and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **111**, 49—67).—The ideal action of an enzyme, which the action of emulsin on salicin resembles, is discussed mathematically. S. S. Z.

The Action of Enzymes under Abnormal Conditions and the alleged Aldehydic Character of Enzymes. ELISABETH RONA (*Biochem. Zeitsch.*, 1920, **109**, 279—289).—The activity of pepsin, trypsin, amylase, emulsin, invertase, and maltase was investigated in the presence of well-known carbonyl reagents in order to ascertain whether enzymes possess an aldehydic character. The results obtained show that, providing that the suitable H-ion concentration is insured, hydrolysis generally takes place in the presence of those reagents. S. S. Z.

Toxic Actions in Enzymic Processes. II. The Inactivation of Saccharase (Invertase) by Organic Substances. HANS VON EULER and OLOF SVANBERG (*Fermentforsch.*, 1920, **4**, 29—63; from *Chem. Zentr.*, 1920, iii, 639—640. Compare A., 1920, i, 689).—The most inactivating substances for saccharase are aniline and *p*-toluidine. The inactivating action of aniline can be partly eliminated by the addition of benzaldehyde or acetone to the inactivated enzyme. It is supposed that the aniline is combined with the saccharase through an aldehyde group, and that the compound of saccharase and aniline has the structure of a Schiff's base.

Other aldehyde reagents, namely, phenylhydrazine, hydroxylamine, semicarbazide, hydrocyanic acid, and sodium sulphite also inactivate the action of the enzyme. Of the amine reagents, some showed an activating influence, others did not. S. S. Z.

Action of Lipase. EMIL ABDERHALDEN and ARTHUR WEIL (*Fermentforsch.*, 1920, **4**, 76—89; from *Chem. Zentr.*, 1920, iii, 643—644).—The action of lipase from cattle pancreas on optically active synthetic fats was studied with the object of ascertaining whether there is a connexion between the structure and configuration of the substrate and the action of the enzyme. It was found that the enzyme was not specific in this respect. From the velocity of the saponification of the various fats, it is concluded that, besides the lipase, which degrades triglycerides, there is no esterase present in the enzyme. The activity of the glycerol extract of the pancreas is weakened by ultrafiltration, but can be reactivated by the addition of the residue retained by the filter. S. S. Z.

Action of Poisons. The Action of Atoxyl on Serum Lipase. P. RONA and E. BACH (*Biochem. Zeitsch.*, 1920, **111**, 166—188).—The susceptibility of serum lipase emanating from different animals to atoxyl varies with the origin of the enzyme. Tributyrin exercises a protective influence on the toxic action of atoxyl. The influence of atoxyl on the kinetics of serum lipase was worked out quantitatively. S. S. Z.

Urease and the Influence of Poisons on its Action. P. RONA and P. GYÖRGY (*Biochem. Zeitsch.*, 1920, **111**, 115—133). —The optimum hydrogen-ion concentration, $P_H = 7{\cdot}3$—$7{\cdot}5$, for the action of soja-bean urease has been confirmed. The accelerating influence of serum on urease could only be recorded in experiments of long duration. On the other hand, no activating action of amino-acids, and retarding action of water and sodium chloride, could be established. The influence of arsenic compounds on urease and lipase has also been studied. S. S. Z.

Action of Poisons. Experiments on the Toxic Effect of ββ′-Dihydroxyethyl Sulphide and its Derivatives on Soja Bean Urease. P. RONA and H. PETOW (*Biochem. Zeitsch.*, 1920, **111**, 134—165).—The toxic effect of the above compounds on the action of soja-bean urease has been studied. Dihydroxydiethyl sulphide and its acetate are not toxic for urease. The sulphone is very slightly toxic. Dichlorodiethyl sulphide influences the hydrogen-ion concentration by making the solution acid, which hinders the action of the enzyme. On rectifying the reaction, however, it still inhibits urease to some extent. Tetrachlorodiethyl sulphide also alters the reaction, but is toxic even when the reaction is regulated. The stability of some of the above derivatives to water was investigated by means of conductivity experiments. S. S. Z.

Additive Reactions of Phosphorus Haloids. I. The Mechanism of the Reaction of the Trichloride with Benzaldehyde. JAMES B. CONANT and ALEXANDER D. MACDONALD (*J. Amer. Chem. Soc.*, 1920, **42**, 2337—2348).—Phosphorus trichloride forms an additive compound with benzaldehyde. The reaction, $C_6H_5{\cdot}CHO + PCl_3 \rightleftharpoons C_6H_5{\cdot}CH{<}^{O}_{PCl_3}$, is reversible, and the factors governing the equilibrium can be expressed in terms of the law of mass action. The values obtained for the equilibrium constant varied from 6·9 to 8·3, the average being 7·4. The additive product reacts with acetic anhydride, and, as in the case of the unsaturated ketones (compare A., 1920, i, 454), the products are acetyl chloride and a mixture of an acid chloride (I) and an anhydride (II).

$$C_6H_5{\cdot}CH{<}^{O}_{POCl} \qquad \left(C_6H_5{\cdot}CH{<}^{O}_{PO}\right)_2O$$

(I.) (II.)

The acid chloride and anhydride are converted by water into *anhydro-α-hydroxybenzylphosphinic acid*, $C_6H_5\cdot CH<\overset{O}{\underset{PO\cdot OH}{|}}$, best isolated in the form of its *barium* salt. The acid or its barium salt only reduces potassium permanganate very slowly. It contains a three-membered, carbon–oxygen–phosphorus ring, and it is suggested that acids of this type should be called *phostonic acids*. When the acid is boiled with water, it is converted into *α-hydroxybenzylphosphinic acid*, $OH\cdot CHPh\cdot PO(OH)_2$, best isolated from ethereal solution as its *aniline* salt, m. p. 201—202° (decomp.).

It is of interest to note that the three-membered ring in the above anhydro-acid is much more stable than the corresponding five-membered ring, $\begin{array}{c}\cdot C\cdot C{:}C\cdot \\ \vdots \quad\;\; | \\ P\text{---}O\end{array}$, obtained with the unsaturated ketones (*loc. cit.*). It is suggested that this exceptional fact may be due to the presence of the ethylene linking in the latter ring.

Benzaldehyde, phosphorus trichloride, and glacial acetic acid react to form acetyl chloride, and the anhydrophosphonic acid together with some hydroxyphosphonic acid. Dilution with water and subsequent evaporation of the solution to dryness converts the anhydro-acid into the hydroxyphosphonic acid. W. G.

Organic Compounds of Arsenic. I. Reaction between the Grignard Reagent and Arsenious Chloride. KAORU MATSUMIYA (*J. Tokyo Chem. Soc.*, 1920, **41**, 868—876).—See A., 1920, i, 777. The correct m. p. of *di-α-naphthylchloroarsine* is 166—167°. K. K.

The Reactions of the Arsines. Condensation of Primary Arsines with Aldehydes. ROGER ADAMS AND CHARLES SHATTUCK PALMER (*J. Amer. Chem. Soc.*, 1920, **42**, 2375—2378). —*n*-Butaldehyde (2 mol.) condenses with phenylarsine (1 mol.) to give *phenyldi-α-hydroxy-*n*-butylarsine*, $AsPh(CHPr\cdot OH)_2$, b. p. 228°/26 mm., D^{30} 1·114, n^{30} 1·686. Similarly, benzaldehyde and phenylarsine give *phenyldi-α-hydroxybenzylarsine*,

$$AsPh(CHPh\cdot OH)_2,$$

m. p. 193°. These condensation products are stable towards dilute acid or alkali or water. W. G.

Hypophosphorous Acid Preparation of Arsphenamine (3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene Dihydrochloride). WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1920, **42**, 2402—2405).—The author confirms the results of Fargher and Pyman (T., 1920, **117**, 370) on the preparation of salvarsan by reduction of 3-amino-4-hydroxyphenylarsinic acid with hypophosphorous acid. The product obtained in this way is relatively non-toxic, and by application of this method toxic arsphenamine can be converted into a relatively non-toxic material, by oxidation and subsequent reduction. The source of the aminohydroxyphenylarsinic acid does not affect the toxicity of the arsphenamine obtained from it. W. G.

Mercury Derivatives of Phthaleins. EDWIN C. WHITE (*J. Amer. Chem. Soc.*, 1920, **42**, 2355—2366).—Of recent years, certain mercurated phthaleins have been found of use in the treatment of genito-urinary infections and of syphilis. The preparation and properties of these compounds are now given. The substitution of mercury is analogous to sulphonation, halogenation, or nitration, and the metal enters the phenolic group of the phthalein molecule in the ortho-position relatively to the hydroxyl or the quinone oxygen. The number of atoms of mercury entering the molecule is limited by the number of such free ortho-positions, and if all four are occupied, as in the case of eosin, no substitution of mercury occurs.

Two general reactions were used for the preparation of these compounds, namely, by the action of yellow mercuric oxide on a solution of a phthalein salt and the action of mercuric acetate on the free phthalein. The second method leads to the maximum degree of substitution in the free ortho-positions, except in the case of phenolphthalein. If carried out in alcoholic solution, an acetoxymercury derivative, ·Hg·OAc, is obtained, but if carried out in aqueous suspension, owing to partial hydrolysis, a mixture of acetoxymercury and hydroxymercury derivatives result. The following compounds are described:

Phenolphthalein gives *hydroxymercuriphenolphthalein*, $C_{20}H_{13}O_4(Hg{\cdot}OH)$, and *triacetoxymercuriphenolphthalein*, $C_{20}H_{11}O_4(Hg{\cdot}OAc)_3$. Fluorescein gives a salt of *dihydroxymercurifluorescein*, $C_{20}H_9O_5Na(Hg{\cdot}OH)_2$; *hydroxymercurifluorescein*; *chloromercurifluorescein*, $C_{20}H_{11}O_5(HgCl)$; and a mixture of *tetrahydroxymercuri-* and *tetra-acetoxymercurifluoresceins* in which the former predominates, and is probably formed by hydrolysis of the latter.

Phenolsulphonphthalein gives the *sodium* salt of *trihydroxymercuriphenolsulphonphthalein*, $C_{19}H_{10}O_5SNa(Hg{\cdot}OH)_3$; *dihydroxymercuriphenolsulphonphthalein*, $C_{19}H_{12}O_5S(Hg{\cdot}OH)_2$; and a mixture of *tetrahydroxymercuri-* and *tetra-acetoxymercuriphenolsulphonphthaleins*, in which, as before, the first-named predominates.

o-Cresolphthalein gives a *diacetoxymercuri*-derivative, $C_{22}H_{16}O_4(Hg{\cdot}OAc)_2$, and dibromofluorescein gives *dibromohydroxymercurifluorescein*, $C_{20}H_9O_5Br_2Hg{\cdot}OH$, which, in the form of its *disodium* salt, has found application under the name of "mercurochrome 220."

For the analysis of these compounds, the acetoxymercury derivatives are distilled with steam in the presence of phosphoric acid, the acetic acid passing over being titrated with standard alkali. For the estimation of mercury, the compounds are decomposed by potassium permanganate and sulphuric acid, the mercury being subsequently precipitated as sulphide and weighed as such.

W. G.

Physiological Chemistry.

Viscosity of Suspensions of Blood Corpuscles. EMIL HATSCHEK (*Kolloid Zeitsch.*, 1920, **27**, 163—165).—A theoretical paper in which it is shown that the formula $\eta' = \eta/(1+k)$ put forward by Hess (this vol., ii, 18) to give the viscosity of a suspension of solid particles, is of the same type as that previously (A., 1911, ii, 98) put forward by the author. This formula leads to exactly the same results if $K\alpha = K^{\frac{1}{3}}$, where α is the factor for converting the actual volume of the suspended particles K into the volume which functions in the process. Several values of α which have been calculated from previously published measurements on suspensions of blood corpuscles show that the values of α calculated from the above expression are in fair agreement. From this it follows indirectly, and also from a very large number of measurements, that the viscosity of suspensions of blood corpuscles, over a wide range of concentrations, is represented by the formula put forward by the author (*loc. cit.*), $\eta' = \eta . A^{\frac{1}{3}}/(A^{\frac{1}{3}} - 1)$, with an accuracy which is greater than the error of observation.

J. F. S.

Blood Gas Analyses. V. The Influence of Alkaline Earths on Hæmoglobin and Cell Colloids. H. STRAUB and KL. MEIER (*Biochem. Zeitsch.*, 1920, **109**, 47—81).—Low concentrations of alkaline earths contain the principle *b* which produces the permeability of erythrocytes by changing or neutralising the charge of the cell colloids. In higher concentrations, these metals contain the antagonistic principle *a*. Calcium does not act in this way like the other members of the group. Michaelis' conception that hæmoglobin is an ampholyte is criticised. S. S. Z.

Blood Gas Analyses. VII. The Influence of Boron, Aluminium, and Lanthanum on Hæmoglobin and the Cell. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1920, **111**, 45—66. Compare A., 1920, i, 200).—Boron, aluminium, and lanthanum in weak concentrations neutralise the charge of hæmoglobin. Although the influence of the above elements is the same, the activity cannot be ascribed to the ions, since lanthanum was used as the easily dissociable chloride, aluminium as the chloride which dissociates only to a small degree, and boron was applied as boric acid, which does not dissociate at all; moreover, these compounds do not obey Schulze's valency rule. It is assumed that the activity is due to the atoms and not to the ions. Experiments with the above compounds on their action on the entire cell were vitiated by the fact that hæmolysis took place. S. S. Z.

Blood Gas Analyses. VIII. The Influence of some Digitalis Substances on the Ion Penetration in Human Erythrocytes. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1920, **111**, 67—82).—Erythrocytes suspended in physio-

logical salt solution containing digitalis substances allow the penetration of ions at a higher acidity produced by carbon dioxide than if the substances were not present. A similar influence was observed to be effected by calcium and other alkaline earth ions in suitable concentrations. Potassium ions, on the other hand, act antagonistically. On the addition of strophanthin, verodigen, and digifolin under certain conditions, the neutralisation of the charge of cell colloids takes place at $P_H = 6{\cdot}49$, $P_H = 6{\cdot}35$, and $P_H = 6{\cdot}32$ respectively. S. S. Z.

Physico-chemical Investigations on Body Fluids. The Character of the Chlorine in Serum and Plasma. I. STEFAN RUSZNYÁK (*Biochem. Zeitsch.*, 1920, **110**, 60—65).—The author confirms Falta and Richter-Quittner's results that, by employing von Korany's method for the estimation of the "total chlorine," higher figures are obtained in plasma than when the chlorine is estimated by methods in which the determination is preceded by the removal of the proteins from the plasma, and that in serum, on the other hand, the same result is obtained by all methods. This, however, is not due to "combined chlorine," but to the higher protein content of the plasma. A similar discrepancy can be observed in serum when the serum content is artificially increased by ultrafiltration. The precipitation methods are therefore suitable only in cases where the protein content is low, as in the case of serum. S. S. Z.

Protein Nitrogen and Residual Nitrogen in the Blood Serum of Various Animals (Vertebrates and Invertebrates). G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 213—218).—The author's investigations show that, whereas the proportion of protein nitrogen in the blood of animals of different types varies in the ratio 1 : 1700, the proportion of residual nitrogen varies only from 1 to 30, or, if reptiles and birds are included, from 1 to 100. This relative constancy of the proportion of residual nitrogen in the blood of all animals, of whatever class, when considered in relation to the wide variation of the protein-content, shows that the fundamental function of the blood consists in the transportation to and from the tissues of the anabolic and katabolic materials (amino-acids, carbamide, ammonia, etc.). Only when the organisation becomes more perfect and the blood assumes other functions does enrichment of the blood in colloidal substances proceed *pari passu* with development of the cardiovascular apparatus. T. H. P.

Presence of Phosphates in Human Blood. XI. Hyperphosphatæmia and "Salt Retention" in Morbus Brightii. JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **111**, 108—114. Compare A., 1920, ii, 506).—A theoretical paper on the phosphates in serum in these diseases. S. S. Z.

Colorimetric Investigations of Tryptophan. I. The Tryptophan Content of Blood Serum and Milk. OTTO FÜRTH and EDMUND NOBEL (*Biochem. Zeitsch.*, 1920, **109**, 103—123).—Voisenet's protein colour reaction is specific for the tryptophan content of the protein. This reaction has been found to be suitable for the estimation of tryptophan in the free or in the combined state without decomposing the protein molecule. Horse serum contains 0·20—0·40% of tryptophan. The globulins which have been examined have shown a higher tryptophan content than the albumins. Caseinogen of cow's milk contains 2% of tryptophan and the lactalbumin from the same source showed a similar content. Proteins of human milk contain much more tryptophan than those of cow's milk. S. S. Z.

The Importance of the Gastric Hydrochloric Acid. L. MICHAELIS (*Biochem. Zeitsch.*, 1920, **111**, 105—107).—A reply to I. Traube (A., 1920, i, 784). S. S. Z.

Gastrin. V. The Chemical Investigation of Substances present in Gastrin. F. C. KOCH, A. B. LUCKHART, and R. W. KEETON (*Amer. J. Physiol.*, 1920, **52**, 508—520; from *Chem. Zentr.*, 1920, iii, 650. Compare A., 1915, i, 190).—Gastrin is obtained from the gastric glands by Pavlov's fistula and by previously injecting secretion-promoting substances. The preparation was coagulated by heat and the filtrate concentrated, neutralised, precipitated with 95% alcohol, and the filtrate obtained by this precipitation also concentrated. The substance was found to be a base of an iminazole character. Gastrin resembles secretin, but is more stable to oxygen. S. S. Z.

New Hypothesis on the Physiological Significance of the Protamines and Histones with respect to Nuclear Metabolism. A. CLEMENTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 298—301).—From considerations on the synthesis of nucleic acid, the chemical constitution of the protamines and histones, and the nutritive value of arginine, the conclusion is drawn that the protamines and histones exert not merely a static function in virtue of their basic character, but also a dynamic function related closely to their chemical constitution. This function appears to be that of immediate reserve substances for the genesis of the pyrimidine bases and purine bases necessary for the synthesis of fresh nucleic acid during the cellular multiplication, or for the synthetic regeneration of the nucleic acid degraded during the normal nucleo-cellular metabolism. T. H. P.

The [Physiological] Action of Calcium. RUDOLF HÖBER (*Pflüger's Archiv*, 1920, **182**, 104—113; from *Chem. Zentr.*, 1920, iii, 564—565).—A deficiency in calcium, as well as an excess of potassium, produces rolaxation in the condition of the cell colloids. This can be counteracted by the addition of various multivalent ions. Calcium deficiency is also responsible for the loosening of

tissues of a different character at the place of contact (that is, nerves and muscles, etc.). In this function, calcium can only be replaced by chemically related substances like strontium and barium. S. S. Z.

Metabolism Studies with Diets Deficient in Water-soluble Vitamin-*B*. WALTER G. KARR (*J. Biol. Chem.*, 1920, **44**, 277—282).—A deficiency of the water-soluble vitamin-*B* does not appear to affect the nitrogen utilisation or metabolism of the dog. J. C. D.

Some Effects of Water-soluble Vitamin on Nutrition. WALTER G. KARR (*J. Biol. Chem.*, 1920, **44**, 255—276).—A relationship was traced in the dog between the desire to partake of food and the amount of the so-called water-soluble vitamin-*B* consumed. Brewers' yeast, bakers' yeast, tomatoes, and milk were investigated as sources of the vitamin-*B*. Brewers' yeast was much more potent than bakers' yeast.

The vitamin content of these supplements is not appreciably lowered by drying at 100°, but heating in an autoclave at 120° for three to four hours causes destruction.

Symptoms of the so-called mammalian polyneuritis were induced in the dogs by the diets deficient in vitamin-*B*. J. C. D.

Chemistry of Whitefish Sperm. VERNON LYNCH (*J. Biol. Chem.*, 1920, **44**, 319—328).—The dried extracted heads of the sperm of whitefish consist of about 70% of nucleic acid and 30% of the protamine, *coregonine*. All the phosphorus is present as nucleic acid, and no iron is present. The combination between the protamine and the nucleic acid is loose, and may be of the amide type rather than of the ammonia type. The analyses agree with the formula $C_{96}H_{160}O_{22}N_{54}(C_{43}H_{51}O_{24}N_{15}P_4)_4$, and this is the probable formula of this chromatin. J. C. D.

A General Colloid Test in Cerebro-spinal Fluid, and the Use of Congo-rubin in particular for this Purpose. HEINRICH LÜERS (*Kolloid Zeitsch.*, 1920, **27**, 177—182).—A general discussion of the use of gold-sols and mastic-sols as an aid to diagnosis of certain pathological conditions of the cerebro-spinal fluid. The author suggests that the congo-rubin sol might constitute a valuable reagent for this purpose, since it is in many respects more easily applied than either of the other sols. The method suggested consists in measuring the protecting action of the colloids in the fluid on the colour change brought about by potassium chloride. Three samples of cerebro-spinal fluid were examined. The method consisted in mixing 1 c.c. of 0·1% congo-rubin solution with 1 c.c. of the fluid, adding 7·65 c.c. of distilled water and 0·35 c.c. of saturated potassium chloride solution, and measuring the time required for the colour change to occur. With normal healthy fluid 41 seconds were required, in a case of locomotor-ataxy 66 seconds, and in a case of syphilis 110 seconds.

J. F. S.

Autolysis. VI. Effect of certain Colloids on Autolysis. H. C. BRADLEY and H. FELSHER (*J. Biol. Chem.*, 1920, **44**, 553—561).—No accelerating action of hydrosols on autolysis of the liver could be detected, and the authors have failed to confirm the findings of Ascoli and Izar (A., 1907, ii, 897; 1908, ii, 121, 713; 1909, ii, 74, 501). When increased autolysis was observed, it was found that acidity could also be detected (compare A., 1917, i, 364). J. C. D.

A Method for the Estimation of Vitamin in Connexion with Determinations of Vitamin in Glandular and other Tissues. FREDERICK K. SWOBODA (*J. Biol. Chem.*, 1920, **44**, 531—551).—The biological test devised by Williams (A., 1919, i, 463) has been developed, and found to be of quantitative value. The vitamin-*B* is found to be present in large quantities in most of the organs of internal secretion which are of developmental importance, and in the liver and kidney. Tissues high in nuclear material were, however, low in vitamin content. J. C. D.

A Complex Nucleic Acid. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, **108**, 147—157).—Quantitative investigations have shown that guanylic acid and pancreas-nucleic acid are present in the pancreas in molecular proportions. On digesting the nucleoprotein from the pancreas with "Pankreatin Merck," and precipitating the products of hydrolysis with crystal-violet, a compound containing guanylic acid and nucleic acid is obtained, the sodium salt of which has $[\alpha]_D^{20}$ about $=50°$. The sodium salt could be quantitatively hydrolysed with alkali hydroxide into sodium guanylate and the sodium salt of pancreas-nucleic acid. The former compound could be salted out in the usual way with sodium acetate. The author therefore concludes that guanylic acid and pancreas-nucleic acid previously established in the pancreas are artificial products of hydrolysis of a complex nucleic acid. S. S. Z.

The Transformation of Energy in the Muscle. I. The Relation of Lactic Acid to the Heat Production and to the Performance of Work in the Muscle in Anærobiosis. OTTO MEYERHOF (*Pflüger's Archiv*, 1920, **182**, 232—283; from *Chem. Zentr.*, 1920, iii, 562).—0·4—0·6% of lactic acid was obtained by extracting frog's muscle made rigid with chloroform. The quantity of lactic acid obtained depended on the time of the year, and was parallel to the "fatigue maximum." The "caloric quotient," that is, gram-cal. per 1 gram of lactic acid, was estimated under different conditions of the muscle. S. S. Z.

The Transformation of Energy in the Muscle. II. The Fate of Lactic Acid during the Recovery Period of the Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1920, **182,** 284—317; from *Chem. Zentr.*, 1920, iii, 562—563).—The formation of lactic acid during rest may be considered as "intramolecular respiration," and one-quarter of the heat only produced in normal

respiration can be accounted for. The accumulation of lactic acid in anærobiosis is three to four times as great as in the transformation of dextrose into lactic acid. In the case of normal respiration, the extra accumulation of lactic acid is prevented. Respiration during rest, and oxidation taking place during the activity of the muscle, may be considered identical processes, which proceed according to the following scheme: (I) hexosediphosphoric (fructosediphosphoric) acid + $2H_2O$ = 2 lactic acid + 2 phosphoric acid; (II) 3 lactic acid + 2 phosphoric acid + $3O_2$ = $3CO_2$ + $5H_2O$ + 1 hexosediphosphoric (fructosediphosphoric) acid.

Details of the calorimetric relation of the two processes are given.

S. S. Z.

The Oxidation of Carotene from Crustacea and the Presence of a Substance in the Oxidation Product which gives a Cholesterol Reaction. J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 980—990; from *Chem. Zentr.*, 1920, iii, 642. Compare A., 1920, i, 680).—Carotene extracted from the integument oxidises slowly at ordinary temperature, but more quickly at higher temperatures, or especially with chromic acid. In the course of the oxidation, the carotene becomes decolorised and the absorption bands in the spectrum disappear. When completely decolorised, it is lævorotatory (α_D −20°), and the m. p. falls according to the degree of oxidation. The oxidation product is stained by osmic acid and Sudan-red, and gives the cholesterol reactions of Salkowski, Liebermann, and Schiff. The pancreas of lobsters and crabs contains much, the blood a little, and the subcutaneous tissue no, cholesterol. The author considers that carotene and cholesterol contain a polycyclic nucleus. S. S. Z.

Bioluminescence. III. The Production of Light by *Luciola vitticollis* is an Oxidation Process. SAKYO KANDA (*Amer. J. Physiol.*, 1920, **53**, 137—149; from *Chem. Zentr.*, 1920, iii, 563. Compare A., 1920, i, 695).—The isolated light organs of the Japanese glow-worm, *Luciola vitticollis*, do not greatest light intensity is obtained in an atmosphere of oxygen, and is controlled by the oxygen content. The production of carbon dioxide from the oxygen used up is demonstrated volumetrically. The presence of water is necessary for the illumination process, which also does not function when the temperature is raised to 50°. On cooling the light is emitted again. S. S. Z.

Bromine and Chlorine Existing Normally in Animal Tissues. A. DAMIENS (*Compt. rend.*, 1920, **171**, 930—933).—The results of analyses of the various organs and tissues of a number of animals, birds, and human beings show bromine to be an invariable constituent. The ratio of bromine to chlorine in the organs of a given animal are sensibly constant within the limits of experimental error. The examination of the thyroid

glands of five dogs does not show any accumulation of bromine in this gland comparable with that of iodine. W. G.

Identification of Bromine in Normal Human Organs. ARNOLD PILLAT (*Zeitsch. physiol. Chem.*, 1919, **108**, 158—164). —Tissues of various organs emanating from human beings (mostly suicides) were examined for bromine by Swarts-Baubigny's and Guareschi's tests. From the results obtained, the author concludes that bromine is not a normal constituent of the human organism. S. S. Z.

The Detection of Selenium in the Human, Animal, and Plant Organisms. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1919, **108**, 38—41).—A reply to Fritsch (A., 1919, i, 191). Selenium is present in the ashes of bones, teeth, and plants in a complex form. It can be extracted from the ash, together with magnesium, by treatment with absolute alcohol. The alcoholic extract is evaporated to dryness, dissolved in aqua regia, and, after removal of the excess of acid, treated with hydrogen sulphide, when a yellow precipitate is obtained containing the selenium; this is dissolved in nitric acid and precipitated with silver nitrate. The presence of selenium in the precipitate can be confirmed as usual. S. S. Z.

Biochemical Studies on Marine Organisms. II. The Occurrence of Zinc. MEYER BODANSKY (*J. Biol. Chem.*, 1920, **44**, 399—407. Compare A., 1920, i, 909).—The constancy of the occurrence of zinc in marine organisms suggests that it is a normal constituent of their tissues. The zinc may be present in excess of its combining power with the proteins of the tissues, or it may exist in part in a loosely combined state, which is disintegrated during dialysis. J. C. D.

A New Method for the Separation of the Highly Unsaturated Fatty Acids in Fish Oils. MITSUMARU TSUJIMOTO (*J. Chem. Ind. Japan*, 1920, **23**, 1007—1010).— The method depends on the ready solubility of the lithium salts of the highly unsaturated acids in acetone containing a little water (95% acetone by volume) and the insolubility or sparing solubility of the saturated and less unsaturated acids in the same solvent. The amounts of the acids obtained by the method are considerably higher than those calculated from the yields of the polybromides. The author assigns the formula $C_{22}H_{34}O_2$, in place of $C_{18}H_{28}O_2$, to clupanodonic acid, which he isolated from Japanese sardine oil. K. K.

The Nature of the Combination of the Chlorine in Urine. A. T. CAMERON and M. S. HOLLENBERG (*J. Biol. Chem.*, 1920, **44**, 239—241).—Chlorine appears to occur in normal urine only as chloride. No confirmation was obtained of the existence of organically combined chlorine or chlorine oxy-acids in urine. J. C. D.

The Biology of Silicic Acid, Alumina, and Iron. M. GONNERMANN (*Zeitsch. physiol. Chem.*, 1920, **111**, 32—35).—The silicon, aluminium, and iron contents of a selection of gall-stones, intestinal, kidney, bladder, and cancer concretions, and benzoar-stones, were determined. S. S. Z.

The Theory of Magnesium Narcosis. ERNST WIECHMANN (*Pflüger's Archiv*, 1920, **182**, 74—103; from *Chem. Zentr.*, 1920, iii, 564).—The expression magnesium narcosis is not justified. Magnesium attacks mainly the "synaptic" tissue which connects nerves and muscles. It also has a paralysing action on automatic organs, like the heart, the stomach, and the intestines. Calcium functions antagonistically to magnesium in the muscle. Cobalt, manganese, nickel, and the complex hexamminecobalt chloride possess the paralysing action, like magnesium. On the other hand, strontium and barium can replace calcium in its antagonistic action. Magnesium and hexamminecobalt contribute to the swelling and disintegration of the cell walls of the roots of plants. Calcium, strontium, barium, cobalt, manganese, and nickel, on the contrary, solidify the cell walls. All the above phenomena can be explained on chemical and colloidal chemical grounds. S. S. Z.

Local Anæsthetics. L. LAUNOY and Y. FUJIMORI (*Compt. rend. Soc. Biol.*, 1919, **82**, 732—736).—The authors compared the toxicity and anæsthetic power of a number of benzoylated derivatives of amino-alcohols of the types (1) $NMe_2\cdot CH_2\cdot CMeR\cdot OH$ and (2) $NMe_2\cdot CH_2\cdot CH_2\cdot CHR\cdot OH$, where R is an aliphatic or aromatic radicle. General toxic action was tested on the frog, the hæmolytic action on rabbit corpuscles, and the anæsthetic action on the sciatic of the frog. The benzoylated derivatives of series (1) were more toxic and had greater anæsthetic power than those of series (2). The C_5-derivatives (amyl alcohols) showed the greatest toxicity and anæsthetic action. In the aromatic series, benzoyl derivatives were more toxic than phenyl derivatives. Hæmolytic action was distinct with C_5-derivatives, and became quite pronounced with C_8-derivatives; it apparently increased with the molecular weight. CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Luminous Radiations on a Nitrogen-fixing Organism. E. Kayser (*Compt. rend.*, 1920, **171**, 969—971).—The organism studied was *Azotobacter agile*. The maximum nitrogen fixation was under the influence of yellow light, the minimum with violet light. The yellow light also gave the maxi

mum soluble nitrogen. Maximum fixation corresponded with maximum disappearance of nutrient carbohydrate and maximum microbic growth. W. G.

Certain Factors that Influence the Production of Acetone by *Bacillus acetoethylicum*. C. F. ARZBERGER, W. H. PETERSON, and E. B. FRED (*J. Biol. Chem.*, 1920, **44**, 465—479).—*Bacillus acetoethylicum* ferments dextrose, sucrose, potato starch, and xylose in a peptone–phosphate mixture, with the production of acetic, formic, and lactic acids, ethyl alcohol, acetone, and carbon dioxide. These products represent from 90 to 95% of the sugar fermented. In a 2% solution, 75 to 80% of the original carbohydrate is fermented within ten to fifteen days.

The optimum condition for the production of acetone is at $p_H=5{\cdot}8$ to $6{\cdot}0$, and the reaction has an important influence on the products formed. An alkaline fermentation kept at about $p_H=8{\cdot}0$ is fermented by *B. acetoethylicum*, with the formation of large amounts of volatile acids and comparatively small amounts of alcohol and acetone. A balance between these three products seems to exist, for an increase in the production of the volatile acids is accompanied by a decreased yield of alcohol and acetone, and vice versa. Acetone is not produced immediately in new cultures, but is formed after several days of fermentation.

The volatile acid formed is composed of about 45% of formic acid and about 55% of acetic acid. Ethyl alcohol is produced in yields of 8 to 25%, depending on the reaction of the medium.

Potato-starch medium, when inoculated with *B. acetoethylicum*, is first liquefied, and then goes through a process of hydrolysis. No reducing sugars have been detected in a fermenting culture of this kind. Cultures previously treated with toluene, or freed from organisms by filtration, also produced similar changes in a starch medium. Traces of reducing sugars were found, and a characteristic red colour was always produced with iodine. The hydrolysis of the starch into dextrin-like substances indicates the liberation of enzymes by the bacterial cell, which function as hydrolytic agents. The negative tests for reducing sugar do not exclude the probability of their formation during bacterial activity, for the sugars may be utilised by the organism as rapidly as they are formed. J. C. D.

The Velocity of Growth of Lactic Acid Bacteria in different Hydrogen-ion Concentrations. OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, **108**, 120—146).—Growth experiments with various strains of lactic acid bacteria were carried out under conditions of different hydrogen-ion concentrations. The optimum hydrogen-ion concentration for *Streptococcus lactis* was found to be $P_H=5{\cdot}5$—$6{\cdot}4$. At $P_H=6{\cdot}5$—$6{\cdot}8$, there was a diminution in the rate of growth of this organism. The optimum reaction for *Bacterium casei* was found to be between $P_H=5$—6. At $P_H=6$—$6{\cdot}4$, the rate of growth diminished. *B. Delbrücki* behaved similarly to *B. casei*. S. S. Z.

Physiology of the Yeast Cell. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **111**, 17—29).—Yeast previously washed with water contains an activated enzyme, "enzyme mirror" (*Fermentspiegel*), which produces fermentation in sugar. If this ferment is not reactivated in the process of fermentation, the fermentation comes to an end, or if the rate of reactivation is slower than the rate of utilisation of the enzyme, the velocity of fermentation diminishes. The latter was found to be the case in the author's experiments. The relation of fermentation to the growth of the yeast, as well as the localisation of the fermenting enzyme in the cell, are discussed. S. S. Z.

Toxic Action in Enzymic Processes. III. The Influence of Copper Sulphate on the Autolysis of the Yeast Cell. OLOF SVANBERG and H. VON EULER (*Fermentforsch.*, 1920, **4**, 90—96; from *Chem. Zentr.*, 1920, iii, 640. Compare this vol., i, 68).—Copper sulphate does not appreciably inhibit the action of saccharase (invertase). On the addition, therefore, of copper sulphate to pressed yeast, autolysis was inhibited, but the saccharase from the treated auto-fermented yeast did not pass more freely into the juice than in the case of the untreated yeast. S. S. Z.

Colloidal Condition of the Proteins in Yeast Extracts. I. Yeast Extract Proteins in Alkaline Solution. Relationship to Biological Processes. A. FODOR (*Kolloid Zeitsch.*, 1920, **27**, 58—69).—Yeast extract is shown to contain an albuminous substance, termed "acid coagulum," which is connected with the ferment action of yeast extract; this substance differs mainly from the other proteins in yeast extract by a great difference in solubility. On account of the difficulty in obtaining this substance in any quantity, its ferment action and properties have been determined in the original extract. The electrical conductivity, viscosity, and hydrogen-ion concentration have been determined at 25°. It is shown that the hydrogen ion changes in concentration with time, and this is attributed to an increased combination with alkali. Hypotheses are put forward to explain the ferment action in biological processes. J. F. S.

Course of Alcoholic Fermentation by Yeast. II. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **110**, 128—132. Compare A., 1920, i, 795).—The concentration of sugar influences the course of alcoholic fermentation rhythmically. S. S. Z.

The Third Form of Fermentation of Sugar as a General Consequence of the Dismutation Influence of Inorganic and Organic "Alkalisers." CARL NEUBERG and WERNER URSUM (*Biochem. Zeitsch.*, 1920, **110**, 193—215. Compare A., 1920, i, 798, 915).—A series of "alkalisers" of organic and inorganic nature have been tested for their influence on alcoholic

fermentation, and it has been found that, independent of the nature of the "alkaliser," the degradation of the sugar takes place according to the equation of the third form of fermentation.

S. S. Z.

Chemically Defined Catalysts in Alcoholic Fermentation. CARL NEUBERG and MARTA SANDBERG (*Biochem. Zeitsch.*, 1920, **109**, 290—329).—Fermentable sugars, keto-acids of the carbohydrate series, aldehydic and ketonic plant bases, quinone and natural dyes, nitro- and nitroso-derivatives, hydroxylamine derivatives, organic and mineral disulphides, polysulphides, thio- and selenious acids, reducible metallic salts and elements, were investigated as to their accelerating capacity on alcoholic fermentation.

S. S. Z.

The Influence of Colloidal Metal Solutions on Lower Organisms and the Reason of this Influence. OLGA VON PLOTHO (*Biochem. Zeitsch.*, 1920, **110**, 1—32).—The behaviour of bacteria, algæ, moulds, higher plants, and lower animals in metal hydrosols was investigated. A decided storage of gold was observed in the case of the moulds kept in colloidal gold solutions. This entrance of the gold into the organisms was observed to be more regular and intensive in the living organisms than in the dead moulds. The storage takes place in the membrane, and the gold is deposited there without entering into chemical combination with the tissue.

S. S. Z.

The Influence of Colloidal Metallic Solutions on Mycelia Transferred from a Different Nutrient Medium. OLGA VON PLOTHO (*Biochem. Zeitsch.*, 1920, **110**, 33—59).—The fixation of metallic colloids by moulds depends on the amount of protective organic colloids present. Fully protected metallic sols are not fixed at all. The storage takes place only in acid, but not alkaline, media. This is explained by the fact that the fixation of the metallic colloids is a condensation process brought about by the neutralisation of the electric charge of the metallic particles by that of the particles of the hydrogel of the membrane of the moulds where the metal is fixed. The charge of the gold particles is negative, that of the particles of the hydrogels depends on the reaction of the medium. The growth of the moulds was not inhibited by gold sols, but was by the colloidal silver and copper solutions.

S. S. Z.

The Reduction of Nitric Acid in Green Cells. OTTO WARBURG and ERWIN NEGELEIN (*Biochem. Zeitsch.*, 1920, **110**, 66—115).—Algæ kept in the dark in solutions containing nitrates produce carbon dioxide by reducing the nitrates, in addition to the carbon dioxide due to respiration. This carbon dioxide is referred to by the authors as "extra-carbon dioxide." Ammonia is also produced from the nitrate at the same time. As this production

of "extra-carbon dioxide" is more sensitive to the influence of hydrocyanic acid than is the ordinary respiration of the plant, it is possible by this means to differentiate between the two processes. Small quantities of phenylurethane inhibit the production of "extra-carbon dioxide." On restricting the quantity of the oxygen, nitrous acid is formed, and a lower production of ammonia is observed. The thermodynamics of the nitrate reduction are discussed. Algæ grown in the light in nitrate solutions produced more "extra-oxygen" than could be expected from the carbon dioxide used up. S. S. Z.

The Utilisation of Nitrates by Moulds for the Production of Nitrogenous Compounds. S. Kostychev and E. Tsvetkova (*Zeitsch. physiol. Chem.*, 1920, **111**, 171—200).—*Aspergillus niger* and *Mucor racemosus* reduce nitrates and nitrites to ammonia, from which they synthesise amino-compounds with the help of sugar. Nitrous acid, ammonia, and amino-compounds have definitely been identified in the intermediate stages. The nitrite nitrogen is converted into ammonia and amino-nitrogen outside the hyphæ, but is not assimilated by them as such in experiments of short duration. The reduction of the nitrate to nitrite can be brought about without the addition of sugar, but the further utilisation of the nitrite takes place, at least in *M. racemosus*, only in the presence of sugar. This reduction of nitrates has been demonstrated by a specially devised method. The old methods employed for such purposes are considered by the authors to be faulty. S. S. Z.

The Formation of Sugar by Moulds from Substances which are not Sugars. S. Kostychev (*Zeitsch. physiol. Chem.*, 1920, **111**, 236—245).—Sugar and alcohol were formed by *Aspergillus niger* from the following substances: *d*-tartaric acid, glycerol, quinic acid, mannitol, and lactic acid. From peptone, on the other hand, sugar was not formed. S. S. Z.

The Character of the Potassium Compounds in Living Plant Tissue. S. Kostychev and P. Eliasberg (*Zeitsch. physiol. Chem.*, 1920, **111**, 228—235).—The total potassium of the plants examined could be extracted with water. On incinerating the extracted residue, the ash was found to be free from potassium. The lead acetate and tannin precipitates were also found to contain no potassium. The aqueous extracts before and after incineration contained the same quantities of the element as estimated by Hamburger's method. Potassium, therefore, unlike other indispensable elements, is not present in the plant, even partly, in combination with organic matter. S. S. Z.

A Method for the Determination of the Molecular Weight Requiring but a Small Quantity of the Substance. II. Yohei Yamaguchi (*J. Tokyo Chem. Soc.*, 1920, **41**, 729—755).—Extending the method proposed by the author (*ibid.*, 1916.

37, 727), the following formula was derived: $n = \Delta T/(K/10)(n = \Delta T/1{\cdot}85$ for aqueous solution), where n represents the concentration of the solution (strictly speaking, the iso-osmotic concentration), ΔT lowering of the freezing point, and K the molecular depression. Using this formula, the author calculated the concentration of many solutions occurring in nature, for example, human blood and the saps of leaves of many plants, obtaining the following results: The concentration of the blood of healthy adults has approximately the same value as that of physiological salt solution. The concentration of the saps of leaves of evergreen trees is generally larger than that of deciduous ones. The order of lowering of the freezing point of saps of pine trees coincides with that of the distribution from the temperate to the frigid zone. The concentration in withered leaves is greater than in green leaves. Tinged leaves have smaller concentration than green leaves for the same period of growth. In deciduous trees, the concentration in autumn is greater than in summer, which corresponds with the increase of sugars that occurs in autumn. In drupaceous leaves, the concentration in the night will presumably be larger than in the daytime. In pine trees, the concentration in winter is greater than in summer. K. K.

Colloidal Chemistry of Wood, its Constituents and their Formation. H. WISLICENUS (*Kolloid Zeitsch.*, 1920, **27**, 209—223).—A theoretical paper in which the constitution of wood and the method of its formation are discussed from the point of view of colloidal chemistry. J. F. S.

Some Proteins from the Mung Bean, *Phaseolus aureus, Roxburgh*. CARL O. JOHNS and HENRY C. WATERMAN (*J. Biol. Chem.*, 1920, **44**, 303—317).—The mung bean contains about 21·74% of protein. Five % sodium chloride solution extracts 19·0% of protein from the finely ground seed. This extract yielded two globulins (designated α and β) by fractional precipitation. The yields were 0·35% and 5·75%, respectively, computed on the basis of the dry material extracted. Traces of albumin were also obtained. On analysis, marked differences were found between the three proteins. The β-globulin contained very little cystine. J. C. D.

Dihydroxyphenylalanine, a Constituent of the Velvet Bean. EMERSON R. MILLER (*J. Biol. Chem.*, 1920, **44**, 481—486). —Following the methods of Torquati (A., 1913, i, 1429) and Guggenheim (A., 1914, i, 49), the author has isolated this amino-acid from the Georgia velvet bean. Evidence of the existence of the same substance in other related beans was obtained, and it is suggested that 3:4-dihydroxyphenylalanine is a characteristic constituent of the seeds of plants of the genus *Stizolobium*.

It is possible that prolonged feeding on velvet beans might cause harmful results, although the pharmacological action of the amino-acid is as yet uncertain. J. C. D.

Function of Alkaloids in Plants. G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 416—420. Compare this vol., i, 408).—It has been found that, unlike salts of quaternary bases, betaine exhibits only slight toxicity for bean plants, but examination of a large amount of a tartaric acid extract of these plants fails to reveal the presence of betaine, although small proportions of choline and trimethylamine are detectable (compare Pictet and Court, A., 1907, i, 954).

Certain of the views expressed by Bernardini (this vol., i, 412) are traversed, and the statement that the seed of the tobacco plant contains no nicotine is denied. T. H. P.

Water-soluble Vitamin-*B* in Cabbage and Onions. BERTHA K. WHIPPLE (*J. Biol. Chem.*, 1920, **74**, 175—187).—Water-soluble vitamin-*B* in cabbage is not destroyed by boiling for thirty to sixty minutes, even when the solution is acid or alkaline.

The vitamin is present in onions, but is not destroyed by boiling. Much of the vitamin is lost in the cooking water in both cases.

J. C. D.

The Effect of Cooking on the Water-soluble Vitamins in Carrots and Navy Beans. ELIZABETH W. MILLER (*J. Biol. Chem.*, 1920, **44**, 159—173).—The yeast method for the quantitative estimation of the vitamin-*B* was employed, and gave trustworthy results (compare, however, de Souza and M'Collum, A., 1920, i, 919). Cooking carrots at 100° for thirty minutes, or at 115° in a tightly packed jar for forty-five minutes, did not decrease the amount of vitamin. Navy beans cooked at 120° for thirty minutes lost some 40% per cent. of their value as a source of vitamin-*B*. The loss was not so great when cooking in 0·5% sodium hydrogen carbonate solution for seventy minutes was carried out. A large proportion of the vitamin was present in the cooking water.

J. C. D.

Occurrence of Chelidonic Acid. EMIL STRANSKY (*Arch. Pharm.*, 1920, **258**, 56—69).—The crystalline precipitate obtained by the fractional precipitation of the cold water extract of *Convallaria majalis* by means of lead acetate solution was identified as the lead salt of chelidonic acid, the occurrence of which has previously only been noticed in *Chelidonium majus*, *Veratrum album*, and *Buphane disticha*. As chelidonic acid is quantitatively converted by boiling milk of lime into 1 mol. of acetone and 2 mols. of oxalic acid, this reaction was utilised for the detection and estimation of the acid in *Convallaria* and other plants in which, on account of its close relationship to oxalic acid, it was thought it might be present. The largest amount found was 2·09—2·18% in the leaves of *Convallaria majalis*. A high percentage, 1·42—1·53, was found in an entirely new source, namely, sabadilla seeds. *Chelidonium majus* contained from 0·14—0·74%, according to the season and the particular part of the plant. In certain *Veratrum sp.*, 0·04—0·39% was found, and traces were indicated

in various other Liliaceous and Amaryllidaceous plants. Physiological experiments indicated that chelidonic acid passes through the animal organism for the most part unchanged. G. F. M.

Botanical Chemical Notes. EDMUND O. VON LIPPMANN (*Ber.*, 1920, **53**, [*B*], 2069—2077).—The formation of malonic acid in the form of its calcium salt has been observed during the fermentation of a solution of sucrose which was allowed to cool in a sugar refinery as a consequence of cessation of work, and to which a considerable quantity of clear lime-water had been added.

The occurrence of chelidonic acid in the young leaves of *Gloriosa superba*, a species of lily indigenous to Java, has been established; the anhydrous acid, which can only be obtained after very cautious desiccation of the hydrated substance, has m. p. 240° when uniformly and not too rapidly heated.

Under certain climatic conditions, coumarin is found in *Melilotus arvensis*; it probably exists in the form of a glucoside, which is hydrolysed by an enzyme, also present in the plant, or by emulsin.

The examination of a viscous gum found in a hole in a mountain ash which had been struck by lightning, is described; the fresh material is almost completely soluble in warm water, but rapidly passes into a resinous substance, which is insoluble in water and cannot be dissolved in alkali; the latter substance has the composition $(C_6H_{10}O_5)_n$, and is optically actice, $[\alpha]_D^{20} > -200°$. The resin cannot be hydrolysed by acids, and is unaffected by invertin, emulsin, etc., or by the fresh sap of the leaves or twigs of the mountain ash; the conjoint action of the latter two, however, leads rapidly to the production of sorbinose, $[\alpha]_D^{20}$ $-42{\cdot}9°$ in aqueous solution.

Melibiose has been isolated from a clear, practically colourless syrup which had exuded on an unusually warm day from an incision in the stem of the mallow; the natural occurrence of this sugar does not appear to have been noticed previously. H. W.

The Alkaloids of Japanese Corydalis Bulb. YASUHIKO ASAHINA and SEIZÔ MOTIGASE (*J. Pharm. Soc. Japan*, 1920, 766—772).—K. Makoshi (A., 1908, i, 825) isolated six alkaloids from *Corydalis decumbens Pers.* (Makoshi gave the name *Corydalis Vernyi* to Japanese corydalis, but this is not correct. Compare Asahina and Fujita, *J. Pharm. Soc. Japan*, 1920, 763). The authors isolated protopine and a substance, m. p. 142°, as non-phenolic alkaloids, and bulbocapnine and a substance, m. p. 175°, as phenolic alkaloids from the same bulb; the latter substance was not isolated by the former investigator. K. K.

Occurrence of Hordenine in Seedlings of Cereals. YOSHITAKA HASHITANI (*J. Tokyo Chem. Soc.*, 1920, **41**, 545—556. Compare A., 1920, i, 360).—The existence of hordenine in radicles or germs of the following cereals, obtained by Tenne's method, was determined either by its isolation or by tests with Millon's

reagent according to a special method. The results were as follows, where (+) means the existence of the substance, (−) the absence, and the numbers show the weight of the substance obtained from 100 grams of air-dried samples: (1) *Hordeum sativum:* (*a*) radicles, 0·07 gram; (*b*) malt, 0·002; (2) *Hordeum sativum* (naked), 0·17; (3) *Triticum vulgare,* (−); (4) *Abena sativa,* (+); (5) *Panicum miliaceum,* 0·24; (6) *Panicum frumentaceum,* (+); (7) *Zea mais,* (+); (8) *Andropogon sorghum,* 0·07; (9) *Panicum italicum,* (+); (10) *Oryza sativum,* (+); (11) *Fagopyrum esculentum,* (−); (12) *Soja hispida,* (−). K. K.

Researches on the Fat-soluble Accessory Substance. IV. Nuts as a Source of Vitamin-*A*. KATHARINE HOPE COWARD and JACK CECIL DRUMMOND (*Biochem. J.*, 1920, **14**, 665—667).—The nuts examined, Brazil, Barcelona, pea, walnut, almonds, and butter nuts, contain relatively small amounts of the vitamin-*A*. J. C. D.

Proximate Analysis of Hardwoods. *Quercus Agrifolia.* W. H. DORE (*J. Ind. Eng. Chem.*, 1920, **12**, 984—987).—Oak wood was analysed by suitable modifications of methods used previously (A., 1920, ii, 453) for coniferous woods; the results obtained were:

	Per cent.
Loss on drying	4·20
Benzene extract	0·50
Alcohol ,,	4·33
Water ,,	3·66
Soluble in cold 5% sodium hydroxide solution	18·71
Cellulose	45·48
Lignin	20·25
Pentosans not otherwise accounted for	1·89
Mannan (residual)	None
Galactan (,,)	1·49
	100·51

The treatment employed for the tissue of coniferous woods (successive extraction with benzene and alcohol) was supplemented by extraction with cold water and cold 5% sodium hydroxide solution; lignin was estimated by König and Becker's hydrogen chloride method. W. P. S.

Factors Influencing Alkaloidal Content and Yield of Latex in the Opium Poppy (*Papaver somniferum*). HAROLD EDWARD ANNETT (*Biochem. J.*, 1920, **14**, 618—635).—Morphine in the poppy is a useless end-product of metabolism. The lactiferous system would seem to represent a means of removing waste products of this nature. J. C. D.

A Chinese Drug "Shê-Chuang-tzu." MANZÔ NAKAO (*J. Pharm. Soc. Japan*, 1920, 685—707).—Opinion has differed as to the plant from which this drug is derived. Working with a Manchurian sample, the author, however, determined it to be

Selinum Monnieri, L. By distillation with steam of the finely powdered fruit, 1·3% of essential oil was obtained, and from this *l*-pinene, camphene, and *l*-bornyl *iso*valerate were isolated.

K. K.

Food Plants of Formosa. III. OTOSABURO OKUMURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 556—587. Compare *ibid.*, 1918, **39**, 983; 1919, **40**, 899).—After determining the percentages of water, ash, crude proteins, protein nitrogen, crude cellulose, fats and oils, soluble non-nitrogenous substances, reducing and non-reducing sugars, dextrin, and starch, and of metallic oxides in the ash in four food plants, the author isolated the following constituents: (1) adenine, arginine, histidine, choline, and trigonelline in Hontei-tau (fruits of *Phaseolus lunatus*, L.); (2) adenine, choline, and arginine in Kium-chan (flowers of *Hemerocallis fulva*, L.); (3) adenine, arginine, and choline in Kowachi (tubers of *Pachyrhizus angulatus*, Rich); (4) adenine, trigonelline, and choline in Be-chi (tubers of *Eleocharis planlaginea*, R. Br.).

K. K.

Aluminium as a Factor in Soil Acidity. JOSE JISON MIRASOL (*Soil Sci.*, 1920, **10**, 153—217).—Sand cultures experiments with sweet clover indicated that, in the absence of some calcium compound, aluminium salts were very toxic to this crop, aluminium nitrate being more toxic than the sulphate. When the ordinary plant nutrients were supplied in a water-soluble form, aluminium hydroxide had no effect on the growth of sweet clover. Calcium carbonate in sufficient amounts corrected the toxicity of aluminium salts, and the toxicity was reduced by the addition of calcium superphosphate.

In the case of three sour silt loam soils, good results were obtained by applying limestone at a rate equal to the lime requirement, and fair crops were also obtained by the application of one ton of superphosphate per acre, and good crops by the application of five tons per acre. The best results were obtained by combined applications of limestone and superphosphate.

When these soils were leached out with a solution of potassium nitrate until the leachings were neutral, the acidity of the soil was reduced 99% and about 59% of the aluminium was removed. Sweet clover grew better on the leached than on the unleached soil. Thus aluminium is apparently the determining factor in the acidity of the soils under examination, but it is possible that in some acid soils iron and manganese may become contributing factors.

In so far as aluminium is a factor in soil acidity, the author considers that Hopkins' method (*U.S. Dept. Agric. Bur. Chem. Bull.*, 1903, **73**, 114) is the best one for soil acidity determinations.

W. G.

Organic Chemistry

The Relative Mobility of Atoms and Groups in Organic Compounds. PIETER J. MONTAGNE (*Chem. Weekblad*, 1920, **17**, 378—382).—A discussion of the question of strong and weak combinations in organic compounds exemplified by reference to the author's researches on the action of alcoholic potassium hydroxide on aromatic ketones of the benzophenone type (compare A., 1908, i, 988; 1913, i, 55; 1917, i, 35, 36, 143). It is pointed out that the mobility and reactivity of any atom or group in a compound depend, not only on conditions within the molecule, but also on the environment, the presence of other reagents, of solvents, catalysts, etc., and the conclusion is drawn that the distribution of affinity within the molecule can be changed by alteration of the environment. S. I. L.

Preparation of Chloropicrin from Picric Acid and Trinitrotoluenes. KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET MCKIE (T., 1921, **119**, 29—33).

Dimethylpropylcarbinol and some of its Derivatives. ANDRÉ DESCHAMPS (*J. Amer. Chem. Soc.*, 1920, **42**, 2670—2672).—Dimethylpropylcarbinol (β-methylpentane-β-ol) is conveniently prepared from acetone and *n*-propyl haloids by the Grignard reaction. It is a somewhat viscous oil, with odour of freshly peeled bark; b. p. 122·5—123·5°/762 mm., $D_{4}^{15.5}$ 0·8350, $n^{15.5}$ 1·4125, m. p. −107° to −109°. The bromide (β-bromo-β-methylpentane), chloride, *benzoate*, $C_3H_7\cdot CMe_2\cdot OBz$, white needles, m. p. 182—183°, and *phenylurethane* (*β-methyl-β-amyl phenylcarbamate*),

$$NHPh\cdot CO_2\cdot CMe_2\cdot C_3H_7,$$

long needles, m. p. 239°, are described. J. C. W.

Catalysis in the Manufacture of Ethyl Ether. HUGO SCHLATTER (*J. Ind. Eng. Chem.*, 1920, **12**, 1101—1102).—The use of anhydrous aluminium sulphate as a catalyst in the manufacture of ethyl ether offers no advantages over those produced by the lead sulphate which is normally present in lead–ether stills, and is actually harmful, since it causes pitting and rapid failure of the coils. W. P. S.

Action of the Alkali Metals on the Ethers. J. DURAND (*Compt. rend.*, 1921, **172**, 70—71).—All the ethers apparently react more or less easily with the alkali metals, giving hydrogen and the metal alkyloxide. The conditions favouring the reaction are: (1) negativity of the groups attached to the oxygen; (2) accumulation of ether functions; (3) rise in temperature; (4) boiling of the liquid; (5) the alkali metal being molten.

Ethyl ether only acts with sodium very slowly, but the action is more rapid with the sodium–potassium alloy at the boiling point of the ether. *iso*Amyl ether reacts readily at its boiling point. Anisole, phenetole, veratrole, and benzyl ethyl ether are all vigorously attacked by sodium, particularly on warming. Phenyl ether also acts on sodium when warmed, but here carbonation takes place, owing to secondary changes. W. G.

Action of Thiodiglycol [$\beta\beta'$-Dihydroxydiethyl Sulphide] on Silver Salts. CHARLES MOUREU and MARCEL MURAT (*Chim. et Ind.*, 1920, **4**, 593—596).—$\beta\beta'$-Dihydroxydiethyl sulphide dissolves easily most of the silver salts, even the iodide. It is not possible to precipitate the whole of the silver chloride from its solution in dihydroxydiethyl sulphide by the addition of water. If present, therefore, it prevents the accurate estimation of chlorides volumetrically either by the chromate or thiocyanate methods of titration with silver nitrate. Dihydroxydiethyl sulphide thus interferes with the estimation of yperite ($\beta\beta'$-dichlorodiethyl sulphide) by titration with silver nitrate of the hydrochloric acid liberated by hydrolysis of the yperite. The errors increase with the amount of dihydroxydiethyl sulphide present. W. G.

The Action of the Chlorides of Sulphur on Substituted Ethylenes. Action of Propylene on Sulphur Monochloride and Synthesis of $\beta\beta'$-Dichlorodi-*n*-propyl Sulphide. SAMUEL COFFEY (T., 1921, **119**, 94—98).

Organic Derivatives of Tellurium. III. Crystallographic and Pharmacological Comparison of the α- and β-Dimethyltelluronium Dihaloids. ISABEL ELLIE KNAGGS and RICHARD HENRY VERNON (T., 1921, **119**, 105—108).

Properties and Constitution of the Group ($O\cdot CCl_3$). ANDRE KLING and DANIEL FLORENTIN (*Compt. rend.*, 1921, **172**, 63—66. Compare A., 1920, i, 8, 213).—In compounds like trichloromethyl chloroformate and hexachlorodimethyl carbonate, complete substitution of the hydrogen atoms in the methyl group by chlorine results in the appearance of abnormal properties. The group $\cdot O\cdot CCl_3$ behaves, not as if it were a product of substitution of the methoxy-group, but rather as if it were constituted by the association of a molecule of carbonyl chloride and an atom of chlorine. Thus with the alcohols these chlorinated esters give reactions of the type $R\cdot O\cdot CCl_3 + 2R'OH = CO(OR')_2 + RCl + 2HCl$, and with aqueous aniline, diphenylcarbamide is obtained.

This is confirmed by an examination of the behaviour of trichloromethyl oxalate and hexachlorodimethyl ether, and it thus follows that, when they act under suitable conditions, the tri- or hexa-chloromethyl esters have a different structure from that of the methyl ester from which they are derived. Structures suggested are $\begin{array}{c}R{-}O{=}CCl_2\\ \vert\\ Cl\end{array}$ or $\begin{array}{c}R{-}O{=}CCl_2\\ \diagdown\diagup\\ Cl\end{array}$ Measurements of the mole-

cular refractions and dispersions of such compounds did not, however, indicate such new linkings. This aptitude to react under a tautomeric form only appears when the carbon atom bearing the three chlorine atoms is directly linked to oxygen. Thus hexachlorodimethyl ketone behaves normally like dimethyl ketone. Chloropicrin slowly decomposes, giving carbonyl chloride and nitrosyl chloride (Gardner and Fox, T., 1919, **115**, 1188).

W. G.

Fractionation of Chaulmoogra Oil. ARTHUR L. DEAN and RICHARD WRENSHALL (*J. Amer. Chem. Soc.*, 1920, **42**, 2626—2645).—In connexion with the treatment of leprosy in Honolulu, the effect of administering the pure ethyl esters of chaulmoogric and hydnocarpic acids is being studied. This has necessitated the development of a scheme for fractionating chaulmoogra oil. The experiments described discuss attempts to separate the mixed fatty acids by crystallisation from alcohol, by means of barium acetate, by the fractional distillation of the mixed ethyl esters under 3—4 mm. pressure, and by fractional distillation of the free acids. The scheme which is finally adopted is as follows. The oil (1500 grams) is saponified by heating with sodium hydroxide (240 grams) and water (1 litre) in a large flask in an autoclave under 15 lb. steam pressure for one hour. The product is diluted with 3—4 litres of hot water, acidified with hydrochloric acid, and the oily acids are washed and cooled (about 1400 grams). The acid mixture is distilled in 1000-gram lots from a 2-litre flask of the Claisen type, with fractionating column devices in the side-tube, exhausted by a mechanical pump, and provided with a special receiver (a sketch is given). The first 350 c.c. which collects are worked up for hydnocarpic acid, the next 300 c.c. are added to the subsequent mixtures of crude acid, and the remaining distillate is treated for chaulmoogric acid. The chaulmoogric acid fraction is crystallised from 80% alcohol (about four times as much solvent as acid), and the hydnocarpic acid fraction is treated in the same way until it melts above 35°, when it is fractionated from light petroleum. The yields from 1000 grams of mixed acids should be at least 50 grams of pure hydnocarpic acid and 100 grams of pure chaulmoogric acid.

J. C. W.

Decomposition of Tartaric Acid by Heat. FREDERICK DANIEL CHATTAWAY and FRANCIS EARL RAY (T., 1921, **119**, 34—37).

Succinyldiacetic Ester. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Annalen*, 1921, **422**, 1—15).—Succinyldiacetic acid has been prepared, because in it occurs the carbon skeleton of the basic derivatives of cocaine in a form particularly suitable for synthetic purposes. The only satisfactory method of preparation is one in which ethyl hydrogen acetonedicarboxylate is the initial material.

The preparation of purified acetonedicarboxylic acid, m. p. 138°, in 58—66% yield from hydrated citric acid and fuming sulphuric acid (20% SO_3) is described. The acid is catalytically and quantitatively converted into acetone by aniline, and, if free from any trace of sulphuric acid, is converted by acetic anhydride into its *anhydride*, $C_5H_4O_4$, prisms, m. p. 138—140° [decomp.; orange-yellow mass (the acid itself remains colourless when fused)], and the mixed *anhydride*, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OAc$, pearly scales, m. p. 102°, the carboxydehydracetic acid of von Pechmann and Neger (A., 1893, i, 398) not being produced.

Ethyl (or methyl) acetonedicarboxylate in ethereal solution reacts with sodium to yield ultimately a product containing more than two atomic proportions of sodium, but with pulverised potassium only a *monopotassio*-derivative, $C_9H_{13}O_5K$, needles, is smoothly obtained; this product is also precipitated when the ester is treated with a very concentrated solution of potassium hydroxide or carbonate. The dipotassio-derivative, $CO(CHK{\cdot}CO_2Et)_2$, described by von Pechmann does not exist; when 50% potassium hydroxide solution, preferably mixed with alcohol (500 c.c. to 900 grams), which prevents the subsequent separation of the mono-potassio-derivative, is shaken with ethyl acetonedicarboxylate at $-5°$, the temperature being finally raised to 25° and ether added, the *dipotassium* derivative, $CO_2Et{\cdot}CH_2{\cdot}C(OK){:}CH{\cdot}CO_2K$ or $CO_2Et{\cdot}CH{:}C(OK){\cdot}CH_2{\cdot}CO_2K$, colourless, rhombic leaflets, is obtained, which is stable, can be crystallised from warm alcohol, is neutralised by one equivalent of acid, develops a red coloration with ferric chloride in neutral solution, yields carbon dioxide and ethyl acetoacetate in warm acid solutions, and by Knorr's method is converted by α-methylaminopropaldehyde into the pyrrole *derivative*, $CO_2H{\cdot}CH_2{\cdot}C{<}\begin{matrix}NMe\text{——}CMe \\ C(CO_2Et){\cdot}CH\end{matrix}$, m. p. 134—135°, which, by heating, yields ethyl 1:2:5-trimethylpyrrole-3-carboxylate.

Ethyl succinyldiacetate (*ββ'-diketosuberate*),

$$C_2H_4(CO{\cdot}CH_2{\cdot}CO_2Et)_2,$$

m. p. 46—47°, colourless prisms 3—4 cm. in length (from alcohol), is obtained by the electrolysis of the potassium ethyl potassio-acetonedicarboxylate described above. The enolic potassium is neutralised by 1·2*N*-oxalic acid at 0°, and the electrolysis is effected in a divided cell with platinum electrodes at 12—14 volts and 3—4 amperes at a temperature between $-5°$ and $+5°$, the inner cell containing the cathode being filled with one-third saturated potassium carbonate solution. Ethyl succinyldiacetate is soluble in 10% sodium hydroxide solution, but the solution rapidly deposits a *sodio*-derivative (with loss of $1H_2O$), $C_{12}H_{15}O_5Na$, colourless prisms, from which, by acidification, the free *enol*, $C_{12}H_{16}O_5$, prisms, m. p. 59·5—60°, is obtained, which exhibits the reactions of a β-ketonic ester. Ethyl succinyldiacetate is readily hydrolysed by concentrated hydrochloric acid to the corresponding *acid*, $C_8H_{10}O_6$, colourless prisms, m. p. 117°, and reacts quantitatively

in warm concentrated methylamine acetate solution to give ethyl 1-methylpyrrole-2:5-diacetate, $NMe<\begin{matrix}C(CH_2\cdot CO_2Et):CH \\ C(CH_2\cdot CO_2Et):CH\end{matrix}$, long, domed prisms, m. p. 163—164°. C. S.

The Stereoisomeric Components of α-Sulphopropionic Acid. A. P. N. Franchimont and H. J. Backer (*Rec. trav. chim.*, 1920, **39**, 751—757. Compare this vol., i, 9).—*r*-α-Sulphopropionic acid may be split into its optically active components by fractional crystallisation of its strychnine hydrogen salt. *Strychnine hydrogen* d-*sulphopropionate*,

$$C_3H_6O_5S,C_{21}H_{22}O_2N_2,H_2O,$$

crystallises in triclinic plates, $a:b=0{\cdot}6861:1$, $\alpha=67°32'$, $\beta=133°4'$, $\gamma=119°15'$, $[M]_D^{20}-72°$; the l-*sulphopropionate* crystallises in monoclinic-sphenoidal prisms having $a:b:c=2{\cdot}1543:1:1{\cdot}5839$, $\beta=62°9'$, $[M]_D^{20}-152°$. Both salts decompose at 245—250°.

Of the two *barium hydrogen* salts, that of the *l*-acid has $[M]_D -41°$ and that of the *d*-acid $[M]_D +41°$, whilst for the normal *barium* salts, $C_3H_4O_5SBa,4H_2O$, that of the *l*-acid has $[M]_D +14°$ and that of the *d*-acid $[M]_D -14°$. d-*Sulphopropionic acid*, $C_3H_6O_5S,H_2O$, has $[M]_D +49{\cdot}5°$, and the l-*acid* has $[M]_D -49{\cdot}5°$. The *d*-acid or its normal potassium salt does not undergo racemisation when heated in solution in a sealed tube at 100° for six hours, but if an excess of potassium hydroxide is added, partial racemisation occurs. When heated at 150° for six hours in a sealed tube, the normal potassium salt in solution undergoes complete racemisation. W. G.

Preparation of Formaldehyde from Ethylene. Richard Willstätter and Max Bommer (*Annalen*, 1921, **422**, 36—46).—Although it is evident from the experiments of Bone and Wheeler (T., 1903, **83**, 1074) and Bone and Coward (T., 1908, **93**, 1197) on the limited oxidation of ethylene by oxygen that destruction of the formaldehyde produced occurs rapidly at high temperatures, yet the authors find that this is a practicable method of preparing formaldehyde provided the concentration of the ethylene and of the formaldehyde is kept low. The results of six experiments are given, of which the best is obtained by passing a mixture of ethylene (19·38%), oxygen (7·58%), and nitrogen (73·04%) at the rate of 1·5 litres in thirteen to twenty-one minutes through a Jena-glass tube (45 cm. by 3 mm.) heated at 585°, the weight percentage of the formaldehyde obtained, calculated on the ethylene consumed, being 109, that is, about half the quantity theoretically obtainable. The concentration of the formaldehyde should not be allowed to exceed 2(vol.)% in the hot gaseous mixture. C. S.

Certain Transformations of Trioxymethylene. Angelo Contardi (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 321—324).—Methylenediphosphoric acid, obtained by the action of concen-

trated phosphoric acid on dry formaldehyde vapour (A., 1910, i, 157), may also be prepared by heating phosphoric acid with the calculated proportion of trioxymethylene in a sealed tube at 140—145°. The salts of this acid do not exhibit the anti-fermentative properties of formaldehyde, and the potassium salt may replace the phosphate in nutrient media for the cultivation of yeasts.

Compounds related to phytin being unobtainable in the above way, the effect of the dark electric discharge on dry formaldehyde vapour at 140—145° has been investigated; the discharge has no action, but prolonged heating of the aldehyde at this temperature results in its conversion into methylal, methyl formate, formic acid, carbon dioxide, water, and Butlerov's methylenitan, the last-named representing 51% of the trioxymethylene employed. Thus the presence of a large amount of water is not, as Loew supposed (A., 1886, 609, 864), necessary in order that substances of the sugar type may be obtained from formaldehyde. Polymerisation of formaldehyde to inositol is, however, not effected in this manner.

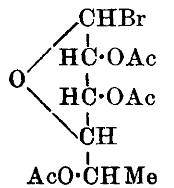
Electrolytic oxidation of inositol in presence of sulphuric acid gives rise to carbon monoxide and dioxide, a little oxalic acid, and a considerable proportion of leuconic acid, $CO<\begin{matrix}CO\cdot CO\\ |\\ CO\cdot CO\end{matrix},4H_2O$, no formaldehyde being detectable. Under similar conditions, phytin yields the same products as inositol.

The principal product of the oxidation of inositol by means of nitric acid is leuconic acid, this result being in disagreement with that of Maquenne (A., 1887, 459). T. H. P.

Acetobromorhamnose and its Application in the Synthesis of Rhamnosides. EMIL FISCHER, MAX BERGMANN, and ARTHUR RABE (*Ber.*, 1920, **53**, [*B*], 2362—2388).—Whereas the application of acetobromoglucose leads almost exclusively to the production of β-glucosides, acetobromorhamnose reacts with methyl alcohol in the presence of silver carbonate to form three different methylrhamnoside triacetates, all of which, again, differ from the product obtained by acetylating the only known methylrhamnoside derived from rhamnose by means of methyl-alcoholic hydrogen chloride. As there is no reason to suppose that the acetobromorhamnose is not homogeneous, or that it does not conform to the butylene-oxide type, it must be argued that the reaction with methyl alcohol is unusually complex. It is suggested that one molecule of the alcohol is primarily taken up by the acetobromorhamnose, through rupture of the oxide ring. Two possibilities are now offered, either the immediate elimination of hydrogen bromide, with formation of a butylene-oxidic methylrhamnoside triacetate, or the intermolecular wandering of an acyl group. Two different rearrangements of the latter type are possible, one leading, by subsequent elimination of hydrogen bromide, to a propylene-oxidic product, the other to one of the

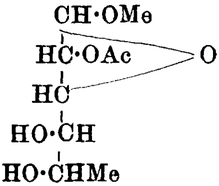
amylene-oxide structure. The fact that the substitution of quinoline for silver carbonate as the acid-fixing medium disturbs the quantitative relationships of the products, and the further discovery that menthol also gives a mixture of rhamnosides, lend support to this suggestion, and it may be inferred that similar phenomena may be encountered in the case of other sugars.

Rhamnose is acetylated by means of acetic anhydride in pyridine solution, giving a syrupy mixture of tetra-acetates, from which a definite crystalline solid, m. p. 99° (see below), occasionally separates. The syrup is converted into an individual *acetobromo-rhamnose* (annexed formula) by means of hydrogen bromide in glacial acetic acid; concentric groups of needles, m. p. 71—72°, $[\alpha]_D^{20}$ $-168{\cdot}97°$ in *s*-tetrachloroethane. Bromine is readily replaced by hydroxyl in this compound by shaking it with silver carbonate in moist acetone. If all the operations, of evaporation and crystallisation (from ether), are carried out quickly and at a low temperature, a *rhamnose α-triacetate* is obtained in hexagonal tablets, m. p. 96—98°. This exhibits mutarotation; for example, alcoholic solutions change from $[\alpha]_D^{21}$ $+28{\cdot}11°$ to $-18{\cdot}6°$ in eight days, when a *β-triacetate*, m. p. 100—115° (decomp.), may be isolated. The isomerisation is hastened by water, pyridine, or rise of temperature, but it is very doubtful whether the β-compound is an individual. The α-triacetate may be acetylated to l-*rhamnose α-tetra-acetate*, which crystallises in concentric groups of prisms, m. p. 98—99°, $[\alpha]_D^{16}$ $+13{\cdot}75°$ in *s*-tetrachloroethane (see above).



α-Methylrhamnoside triacetate, prepared by acetylating the methylrhamnoside obtained directly from rhamnose, crystallises in thin, glistening leaflets, m. p. 86—87° (corr.), $[\alpha]_D^{16}$ $-53{\cdot}66°$ in *s*-tetrachloroethane. The products obtained from acetobromo-rhamnose, methyl alcohol, and silver carbonate, however, consist of needle-like crystals, cubical forms, and a syrup, which are separated by means of solvents (alcohol and light petroleum) and mechanical sorting. *β-Methylrhamnoside triacetate* crystallises from dilute alcohol in very long, thin prisms, m. p. 151—152° (corr.), $[\alpha]^{18}$ $+45{\cdot}73°$ in *s*-tetrachloroethane; *γ-methylrhamnoside triacetate* crystallises in stout prisms, m. p. 83—85°, $[\alpha]_D^{16}$ $+28{\cdot}05°$, in *s*-tetrachloroethane, and is much more soluble in ether and light petroleum; *δ-methylrhamnoside triacetate* is a viscous syrup, b. p. about 150°/0·2 mm., $[\alpha]_D$ $+32$—$34°$ in *s*-tetrachloroethane. These isomerides behave differently towards alkaline hydrolytic agents. The α-, β-, and δ-forms lose three acetyl groups in the normal way, giving the methylrhamnosides [α-, m. p. 109°, $[\alpha]_D$ $-67{\cdot}2°$ in water; *β-methylrhamnoside*, long, felted needles, m. p. 138—140° (corr.), $[\alpha]_D^{20}$ $+95{\cdot}39°$ in water]. The γ-triacetate, however, only loses two acetyl groups when treated with sodium hydroxide, warm baryta, alcoholic ammonia, or even liquid ammonia, the product

being γ-*methylrhamnoside acetate*, probably of the annexed formula, prisms, m. p. 143—144° (corr.), $[\alpha]_D^{16}$ +15·7° in water. This acetate is hydrolysed to rhamnose even by 0·01*N*-hydrochloric acid, and it yields the γ-triacetate on re-acetylation. The occurrence of such a steric hindrance to hydrolysis suggests that the number of acyl or methyl groups which can be introduced or removed from carbohydrates or their derivatives, especially in the case of the polysaccharides, does not necessarily afford conclusive evidence as to constitution.



Substituting quinoline for silver carbonate in the reaction between acetobromorhamnose and methyl alcohol, the authors obtained no β-triacetate, but much of the γ-compound and syrup. Menthol gives a number of products, from which α-l-*menthylrhamnoside diacetate*, $C_6H_9O_4(OAc)_2\cdot O\cdot C_{10}H_{19}$, has been isolated in needles or bundles of prisms, m. p. 134—135° (corr.), $[\alpha]_D^{11}$ +13·3° in alcohol. The syrup left after separating this distils at about 180—190°/0·25 mm., and both the α-diacetate and the distillate may be hydrolysed by alcoholic ammonia to definite l-*menthylrhamnosides*; α-, microscopic prisms, m. p. 114—115° (corr.), $[\alpha]_D^{20}$ −7·48° in alcohol; β-, m. p. 164—166°, $[\alpha]_D^{23}$ −131·3° in alcohol. J. C. W.

The Individuality of Erythrodextrin. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1920, **42**, 2673—2678).—Dextrins which give deep red colours with excess of iodine water, preceded by little or no blue colour, are the best as sources of erythrodextrin, since much of the latter is lost if the addition of dilute alcohol to a dextrin solution causes a large precipitate of the blue-forming amylodextrin. After precipitating the amylodextrin, the further addition of alcohol continues to furnish small crops of spheroids, which are thought to be the same substance as that forming the cell walls of starch, namely, amylocellulose. The heavy liquids subsequently precipitated by alcohol contain the erythrodextrin and also amylocellulose. The addition of ammonium sulphate to the liquid causes separation of the erythrodextrin in a much purer form, which can be rapidly desiccated. Systematic tests of the heavy liquids were carried out by drying them over calcium chloride and determining (1) the polarisation, (2) the colour reaction with iodine (Lovibond scale), (3) the digestibility with saliva to the achromic point, and (4) the reducing power towards Benedict's solution. The ratio between (2) and (4) is fairly constant, and it may be assumed that both give a fair measure of the amount of erythrodextrin present. J. C. W.

The Contrary Action of Soluble Chlorides and Sulphates on Starchy Materials. H. COURTONNE (*Compt. rend.*, 1920, **171**, 1168—1170).—In the presence of soluble chlorides, starch is slowly

converted at the ordinary temperature into a gelatinous mass of amylopectin, which is, in turn, converted into soluble starch if the mixture is heated at 115°. The ease with which these changes take place depends on the solubility of the chloride and the concentration of the solution. A saturated solution of magnesium chloride is the most effective.

Sulphates, on the other hand, retard this change. In the presence of a saturated solution of magnesium sulphate, the starch grains show no sign of swelling, even when heated at 115°, and there is no formation of amylopectin. W. G.

The Chemistry of the Polysaccharides. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **112**, 55—60).—The statement made by the authors in a previous communication (A., 1920, i, 713), that sugar is not formed by the action of diastase on polysaccharides, is not correct. By improved technique, the authors now ascertain that sugar is formed. Ten to twenty % of alcohol-soluble sugar only was established after the hydrolysis of starch by diastase; the residue left behind after the alcoholic extraction did not give the iodine reaction. On digesting the unsaccharified residue of three different polysaccharides with fresh diastase, quantities of sugar were obtained which were of the same order of magnitude as those obtained from the first digestion. The unhydrolysed residues were dissolved in water, treated with 33% potassium hydroxide, precipitated with alcohol, neutralised, and finally washed with alcohol. The substances from the digested polysaccharides thus obtained gave the characteristic colour reactions with iodine. This is explained by the fact that, previous to saccharification, diastase disperses the substrate. The subsequent treatment with alkali and alcohol changes the condition of the surface and brings about the reappearance of the iodine reaction.

S. S. Z.

The Solubility of Cellulose in [Solutions of] the Salts of the Alkali and Alkaline Earth Metals. R. O. HERZOG and F. BECK (*Zeitsch. physiol. Chem.*, 1920, **111**, 287—292).—The solubility of cellulose in the concentrated solutions of the above salts is a function of the hydration of the ions of the respective salts. S. S. Z.

The Methylation of Cellulose. III. Homogeneity of Product and Limit of Methylation. WILLIAM SMITH DENHAM (T., 1921, **119**, 77—81).

Methylamines from Methyl Alcohol and Ammonium Chloride. W. D. TURNER and A. M. HOWALD (*J. Amer. Chem. Soc.*, 1920, **42**, 2663—2665).—Methylamines are only produced in traces when methyl alcohol is heated with ammonia or ammonium chloride in steel tubes, even at 303°, but good results are obtained if zinc chloride is used as a dehydrating agent. For example, a mixture of ammonium chloride (1 mol.), zinc chloride (1·5), and

methyl alcohol (12), heated at 303° for eight hours, gave yields of 55·0, 7·5, and 1·86%, respectively, of mono-, di-, and tri-amines, calculated on the amount of ammonium chloride. The bases were estimated by Bertheaume's method (A., 1910, ii, 663).

J. C. W.

Dimethyldiacetonalkamine [Methyl-β-dimethylamino*iso*-butylcarbinol] and Dimethyldiacetonamine. HANS ROLFES (*Ber.*, 1920, **53**, [*B*], 2203—2206).—Methyl-β-dimethylamino*iso*butyl-carbinol (Kohn, A., 1904, i, 378) is best obtained by heating methyl-β-amino*iso*butylcarbinol with formaldehyde and formic acid, according to the equation $NH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH + 2CH_2O + 2CH_2O_2 = NMe_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH + 2H_2O + 2CO_2$. It has b. p. 75—83°/21 mm., forms a *benzoate*, b. p. 175—180°, and may be oxidised by means of chromic acid to dimethyldiacetonamine, $NMe_2\cdot CMe_2\cdot CH_2\cdot COMe$. This is very volatile in ether, decomposes readily on heating into mesityl oxide, forms an oxime, m. p. 35—44°, and *picrate*, m. p. 154—155°, and thus conforms with the description given by Götschmann (A., 1879, 1035) and Kohn (A., 1904, i, 18), whereas the so-called dimethyldiacetonamine obtained by Hess by the action of excess of formaldehyde without formic acid on methyl-β-amino*iso*butylcarbinol could be distilled, and gave a picrate with m. p. 183°. Hess's product (A., 1916, i, 124) is probably represented by the formula

$$NMe{<}\begin{matrix}CMe_2\cdot CH_2\\CH_2\text{——}O\end{matrix}{>}CHMe.$$

J. C. W.

Constitution of Methyloxaluric Acid. ROBERT BEHREND and GUSTAV HÄRTEL (*Annalen*, 1921, **422**, 74—109).—The constitution of the methyloxaluric acid obtained by the oxidation of 1:4- or 3:4-dimethyluracil is not determined by Behrend and Grünewald's demonstration (A., 1902, i, 834; also Henkel, A., 1911, i, 159) that methylparabanic acid is the intermediate product, since this acid can yield methyloxaluric acid of the formula (I) $NHMe\cdot CO\cdot NH\cdot CO\cdot CO_2H$ or (II) $NH_2\cdot CO\cdot NMe\cdot CO\cdot CO_2H$. The authors have made several unsuccessful attempts to synthesise the acid, and have therefore been compelled to fall back on fission experiments to obtain definite evidence of its constitution. The fission of acetylated methyloxaluric acid by alkali would differentiate between formulæ (I) and (II) only if *as*-acetylmethylcarbamide was the fission product. This, unfortunately, is not the case, the chief product of the action of acetic anhydride at 100° or at the b. p. on methyloxaluric acid being methylparabanic acid or *acetylmethylparabanic acid*, leaflets, m. p. 182—184°, but the fact that in the case of ethyl methyloxalurate the action of acetyl chloride results in the formation of a little ethyl acetyloxamate and ethyl oxamate, together with methylparabanic acid, is some

evidence in favour of formula (I), since an ester of formula (II) would have given ethyl acetylmethyloxamate. C. S.

Behaviour of Mercuric Fulminate with various Solvents. A. LANGHANS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1920, **15**, 219—221, 227—229, 235—237).—The behaviour of solutions of mercuric fulminate in various solvents has been investigated. In potassium cyanide, a small organic residue, derived from impurities, remains. The filtrate yields pure, white fulminate on precipitation with nitric acid. Potassium cyanide solutions are unstable, and, on keeping, develop a white sediment at the surface; the colour of the solutions changes to reddish-brown and reddish-violet on boiling, and, after prolonged keeping, they can no longer be precipitated by nitric acid. No double salts, except with ammonium thiocyanate, can be obtained from the solution. Aqueous ammonia (22%) dissolves fulminate, and yields white, columnar crystals on evaporation; these become opaque if treated with water. Complete decomposition of the solution takes place after twelve hours, with formation of variously coloured sediments, in which no mercuric fulminate can be detected; these are found to consist of reduction products. The ammonia solution when mixed with ammonium thiocyanate yields a double salt. Mono-, di-, and tri-methylamine dissolve mercuric fulminate, with separation of mercury. In the first case, fern-shaped masses of needles are obtained on evaporation, but individual crystals are produced from the di- and tri-methylamine solutions; in every case, the crystals consist of pure fulminate. The solutions in mono- and di-methylamine decompose on keeping, and assume a dark brown and pale yellow colour respectively. The trimethylamine solution decomposes, with separation of metallic mercury. Sodium thiosulphate is a solvent for fulminate, and small crystals separate from the solution; at the same time, solution is accompanied by decomposition. In aniline, fulminate dissolves without violence if the solvent is in excess, but metallic mercury separates, and aniline cannot therefore be regarded as a true solvent. On the other hand, with pyridine, cubical crystals of pure fulminate may be obtained. Water precipitates fulminate from a pyridine solution. The solutions are fairly stable; after keeping for twenty hours, the fulminate, precipitated by addition of water, although yellow, was still of considerable purity. Some separation of mercury which takes place during solution in pyridine is ascribed to its reaction with organic impurities, and not to decomposition of the fulminate itself.

Sodium xanthate dissolves fulminate slightly and forms additive products; the solution decomposes on keeping. Hot acetone and alcohol dissolve small amounts of mercuric fulminate; acetic esters dissolve only traces. In benzene it is almost insoluble; it is quite insoluble in chloroform, glycerol, epichlorohydrin, linseed oil, turpentine, and ethyl nitrate.

When a solution of mercuric fulminate in hydrochloric acid is titrated with potassium iodide, the mercuric iodide first dissolves, and is then precipitated, the demarcation being sufficiently sharp. By the use of a correction factor, accurate results can be obtained.

W. J. W.

ψ-Thiohydantoin. ERNST SCHMIDT (*Arch. Pharm.*, 1920, **258**, 226—250).—The elimination of sulphur from ψ-thiohydantoin by means of mercuric oxide (Volhard, this Journ., 1873, 880; compare Maly, *ibid.*, 1874, 684; Mulder, *ibid.*, 1875, 446) is extremely slow, being incomplete even after four weeks at 100°. Oxalic acid and ammonia were the sole products recognised, but guanidine and oxalic acid are obtained when the reaction is carried out at the ordinary temperature for four months in presence of aqueous or alcoholic ammonia. Since the same products are produced, but more rapidly, from glycocyamidine under these conditions, the failure to obtain this compound from ψ-thiohydantoin is accounted for. Creatinine similarly gives oxalic acid and methylguanidine. By the action of ammoniacal mercuric chloride on ψ-thiohydantoin, or of ammonia on its silver salt, or on the *basic lead* salt ($C_3H_2ON_2SPb,PbO$, yellow precipitate; compare Mulder, *loc. cit.*), the above products were obtained, with a little carbamide. This, however, preponderates when ammonia acts on a mixture of the base with silver carbonate, apparently owing to the preliminary formation of hydantoin, since this is easily converted into carbamide and oxalic acid under the conditions employed. By the action of cold aqueous barium permanganate, there resulted carbamide, oxalic acid, sulphuric acid, and a *sulphonic acid*, $C_3H_4O_4N_2S$, needles [*barium* salt, $(C_3H_5O_5N_2S)_2Ba$, needles; *silver* salt, $C_3H_2O_4N_2SAg_2$, leaflets], from which the sulphur atom is eliminated as sulphuric acid with considerable difficulty by hydrochloric or nitric acid. When thiourea is oxidised by barium permanganate (compare Maly, *loc. cit.*), the yield of carbamide is only moderate, owing to formation of ammonium sulphate. ψ-Thiohydantoin is converted into its oxime (Maly, *loc. cit.*; Andreasch, A., 1886, 226) by treatment with sodium nitroprusside and sodium hydroxide, and the same applies to ε-methylthiohydantoin, but sulphur is easily removed from this compound in aqueous or alcoholic solution by the action of mercuric oxide, especially in presence of ammonia. Methyl- and dimethyl-ψ-thiohydantoins resemble the parent compound in their colour changes with sodium nitroprusside.

An *aurichloride*, $C_3H_4ON_2S,HAuCl_4$, yellow needles, which sinters at 150—160°, but does not melt at 250°, is produced when ψ-thiohydantoin is treated with gold chloride in presence of hydrochloric acid. By solution in hot dilute hydrochloric acid, this salt is converted into a second *aurichloride*, $C_3H_4ON_2S,AuCl_3$, yellow, opaque crystals, which sinter without melting at 250°.

J. K.

Some Propionitriles with Mixed Function. CHARLES MOUREU and RALPH L. BROWN (*Bull. Soc. chim.*, 1920, [iv], **27**, 901—909).—*β-Bromopropionitrile*, b. p. 92°/25 mm., D_4^0 1·6452, D_4^{20} 1·6152, n_D^{20} 1·1470, may readily be prepared by the action of hydrogen bromide on acrylonitrile. On hydrolysis with hydrobromic acid it yields β-bromopropionic acid.

α-Bromopropionitrile, b. p. 59°/24 mm., D_4^0 1·5808, D_4^{20} 1·5505, n_D^{20} 1·4585, is prepared by dehydrating α-bromopropionamide by heating it with phosphoric oxide. It gives an unstable *hydrobromide,* CHMeBr·CN,HBr, m. p. 64—65°, which, by the action of water, is converted into di-α-bromopropionylimide.

αβ-Dibromopropionitrile, prepared by the action of bromine on acrylonitrile, has b. p. 106—107°/22 mm., D_4^0 2·174, D_4^{20} 2·140, $n_D^{20\cdot2}$ 1·5452.

A detailed account of the preparation of β-hydroxypropionitrile from ethylene chlorohydrin, and of the purification of the latter compound, is given. W. G.

Preparation of certain Derivatives of *cyclo*Hexane. A. E. OSTERBERG and E. C. KENDALL (*J. Amer. Chem. Soc.*, 1920, **42**, 2616—2626).—The preparation of *cyclo*hexane derivatives on a fairly large scale is described. *cyclo*Hexane and *cyclo*hexanol are produced by the reduction of benzene and phenol, respectively, by hydrogen at 115—120 atm. pressure in steel bombs heated at 250°, nickel being used as a catalyst. *cyclo*Hexanone is obtained by oxidation of *cyclo*hexanol with chromic acid mixture, and 2-chloro*cyclo*hexanone by chlorination in the presence of calcium carbonate and water. *cyclo*Hexylamine is prepared by reducing *cyclo*hexanoneoxime with sodium and alcohol. *cyclo*Hexene is prepared by distilling *cyclo*hexanol with sulphuric acid or by treating it with phosphorus trichloride. 2-Chloro*cyclo*hexanol is formed by the action of hypochlorous acid solution on *cyclo*hexene, and is readily converted by warming with alcoholic ammonia into 2-*amino*cyclo*hexanol*, rosettes, m. p. 65°, b. p. 212°/760 mm. or 104°/7 mm. (*hydrochloride*, m. p. 175°; *hydriodide*, m. p. 187°; *hydrobromide*, m. p. 191°; *carbonate*, m. p. 139°; *sulphate*, not molten below 250°). 2-*Chloro*cyclo*hexylamine* is obtained by the action of phosphorus pentachloride on a dry solution of 2-amino-*cyclo*hexanol in chloroform at 0°; it is a colourless oil, b. p. 85°/15 mm., and forms an *acetyl* derivative, m. p. 88°, and a *chloroacetyl* derivative, m. p. 111°. The last compound is converted into 2-*chlorocyanoacetyl*cyclo*hexylamine*, $C_6H_{10}Cl\cdot NH\cdot CO\cdot CH_2\cdot CN$, m. p. 139°, by boiling with sodium cyanide solution, and this may be hydrolysed to the malonic ester, and ultimately to N-2-*chloro*cyclo*hexylmalonamic acid*, $C_6H_{10}Cl\cdot NH\cdot CO\cdot CH_2\cdot CO_2H$, m. p. 132°. In a similar manner are prepared 2-*bromo*cyclo*hexylamine*, its *hydrochloride*, needles, m. p. 168°, and its *acetyl* derivative, m. p. 103—104°. J. C. W.

Decomposition of Nitric Acid in Organic Nitrations. F. O. RICE (*J. Amer. Chem. Soc.*, 1920, **42**, 2665—2670).—Some experiments on the nitration of phenol are described, with special reference to the gases evolved, the fate of the nitric acid, and the yield of picric acid. It is found that in nitrations with more dilute nitric acid, as much as 25% may be reduced to nitrous oxide and nitrogen, the presence of iron salts accelerating this reduction. There is a close parallel, therefore, between the action of metals and phenol on nitric acid. By keeping the temperature well below 100°, especially at the commencement of the reaction, the reduction to the lowest stages may be avoided, but some oxides of nitrogen are always produced. Best results are obtained by sulphonating the phenol almost to the disulphonate stage with 96% sulphuric acid, and then nitrating at about 30—40° with the mixed acids. [See also *J. Soc. Chem. Ind.*, 1921, 100A.] J. C. W.

The Three Tetrachlorobenzenes, Pentachlorobenzene, and Hexachlorobenzene; their Reaction with Sodium Methoxide. A. F. HOLLEMAN (*Rec. trav. chim.*, 1920, **39**, 736—750. Compare A., 1918, i, 216).—[With C. VAN DER HOEVEN.]—1 : 2 : 4 : 5-*Tetrachlorobenzene*, m. p. 138°, may be obtained, together with an oily product, by the direct chlorination of benzene in the presence of powdered iron as a catalyst. The preparation is much simplified if *p*-dichlorobenzene is the starting point. Heated in a sealed tube at 180° with sodium methoxide, it yields 2 : 4 : 5-*trichloroanisole*, m. p. 70°, together with some 2 : 4 : 5-*trichlorophenol*, m. p. 66°, giving a *benzoate*, m. p. 92°.

When 2 : 4 : 6-trichloroaniline is diazotised and the product submitted to the Sandmeyer reaction with copper sulphate, sodium chloride, and copper powder, 1 : 2 : 3 : 5-*tetrachlorobenzene*, m. p. 51°, is obtained, which with sodium methoxide yields 2 : 3 : 5-*trichloroanisole*, m. p. 82°, and 2 : 3 : 5-*trichlorophenol*, which gives a *benzoate*, m. p. 103°. When 3 : 4 : 5-trichloroaniline is diazotised and the product boiled with water, 3 : 4 : 5-*trichlorophenol* is obtained, giving a *benzoate*, m. p. 118—119°.

[With C. VAN DER HOEVEN and F. E. VAN HAEFTEN.]—When 3 : 6-dichloro-1 : 2-dinitrobenzene is heated on a water-bath with alcoholic ammonia, 3 : 6-dichloro-2-nitroaniline is obtained, and if this is diazotised in concentrated hydrochloric acid solution, and the resulting product submitted to the Sandmeyer reaction, 1 : 2 : 3 : 4-*tetrachlorobenzene*, m. p. 47·5°, is obtained. When this substance is treated with sodium methoxide, it gives 2 : 3 : 6-*trichlorophenol*, m. p. 55°, giving a *benzoate*, m. p. 90°, and 2 : 3 : 4-*trichloroanisole*, which could not be obtained crystalline, but when heated with hydrobromic acid gave 2 : 3 : 4-*trichlorophenol*, isolated as its *benzoate*, m. p. 141°. The last phenol was also obtained from 2 : 3 : 4-trichloroaniline by diazotisation and subsequent decomposition of the diazo-compound.

[With C. VAN DER HOEVEN.]—By diazotisation of 2 : 3 : 5 : 6-tetrachloroaniline, the product being submitted to the Sandmeyer reac-

tion, *pentachlorobenzene*, m. p. 86°, was obtained. When this compound is treated with sodium methoxide, it yields 2:3:5:6-*tetrachlorophenol*, m. p. 115°, giving a *methyl ether*, m. p. 88°, together with some 2:3:4:5-*tetrachlorophenol*, isolated as its *benzoate*, m. p. 110°.

Hexachlorobenzene, m. p. 226°, was best obtained by the further chlorination of the oily by-product obtained in the preparation of 1:2:4:5-tetrachlorobenzene (see above). With sodium methoxide it gave pentachloroanisole, m. p. 186°.

The reactivity of the chlorobenzenes with sodium methoxide increases with the number of chlorine atoms in the molecule, reaching a maximum with 4 atoms present, and then diminishing slightly. The chlorine atoms in the meta-position to other chlorine atoms are most readily replaced in this reaction. W. G.

The Replacement of Halogen attached to a Ring Carbon Atom by other Substituents. II. Replacement of Halogen by OH, SH, and SeH. KARL W. ROSENMUND and HERBERT HARMS (*Ber.*, 1920, **53**, [*B*], 2226—2240. Compare A., 1920, i, 44).—Copper is found to be an active catalyst in promoting the conversion of aromatic halogen compounds into phenols, by means of neutral salts of weak acids, and in the replacement of halogen by sulphur and selenium by means of thiocyanates or selenocyanates.

Replacement of Halogen by Hydroxyl.—When the halogen compound is heated with the salt of a weak acid, a phenol ester is formed, which is then hydrolysed, and provided that an alkali is present to neutralise the liberated acid, the process continues to the end. Thus, potassium *o*-chlorobenzoate, when heated with sodium acetate, water, and a trace of cupric acetate at 140—150°, gives an 83% yield of salicylic acid, or with borax instead of sodium acetate, a 55% yield. If fused with a low-melting mixture of potassium and sodium acetates (2 : 1·4, m. p. 226°) and a trace of copper bronze, at 245—255°, the product is, however, *o*-phenoxybenzoic acid. Sodium *o*-bromobenzoate also yields salicylic acid when heated with sodium *β*-naphthalenesulphonate, water, and copper powder under reflux, the mixture being kept neutral by the occasional addition of sodium carbonate. Bromobenzene gives a 50% yield of phenol when heated with sodium acetate, water, alcohol, cupric acetate, and calcium carbonate at 220—280°, or a 25% yield if borax is substituted for the sodium acetate and calcium carbonate.

Replacement of Halogen by Sulphur.—When bromobenzene, cuprous thiocyanate, and pyridine are heated at 180°, the chief products are benzonitrile and diphenyl mono-, di-, and tri-sulphides.

p-Bromotoluene, cuprous thiocyanate, and moist pyridine, when heated at 220—250°, yield *p*-toluonitrile and di-*p*-tolyl mono- and tri-sulphides. The disulphide so readily changes into mono- and tri-sulphides when heated that it cannot be isolated. *o*-Bromotoluene gives *o*-toluonitrile, and di-*o*-tolyl mono- and tri-sulphides. In these experiments the trisulphides were not isolated as such, but

the mixtures containing them were treated with zinc dust and aqueous alcoholic hydrogen chloride until the trisulphides were reduced to mercaptans, when the products were dissolved in chloroform and the solutions were shaken with sodium hydroxide to separate the thiols from the mono-sulphides.

In a similar manner, *o*-chlorobenzoic acid has been converted into *2:2′-dicarboxydiphenyl sulphide* [*diphenyl-sulphide-di-*o*-carboxylic acid*], $S(C_6H_4\cdot CO_2H)_2$, m. p. 230°. *o*-Bromobenzoic acid, however, is more reactive, and when dissolved in 0·5*N*-sodium hydroxide and boiled with potassium thiocyanate and copper powder, yields *diphenyl-disulphide-di-*o*-carboxylic acid*, $S_2(C_6H_4\cdot CO_2H)_2$, m. p. 288·5°. *p*-Bromobenzoic acid, on the other hand, does not suffer change under these conditions, but when a solution in sodium hydroxide is heated with potassium thiocyanate, cuprous thiocyanate, and a little barium peroxide (to oxidise the thiol) at about 200°, *4:4′-dicarboxydiphenyl sulphide* [*diphenyl-sulphide-di-*p*-carboxylic acid*], m. p. 315°, and diphenyl disulphide are formed.

α-Bromonaphthalene and 2-bromoanthraquinone give chiefly di-α-naphthyl sulphide and di-2-anthraquinonyl sulphide respectively.

The reactions appear, therefore, to be rather complex. It may be assumed that the primary product is the thiocyanate, $RX \longrightarrow R\cdot SCN$. This may lose sulphur, especially in the cases where dry pyridine is the medium, or be hydrolysed to the thiol, $R\cdot SCN + 2H_2O \longrightarrow R\cdot SH + CO_2 + NH_3$. The thiol may then be oxidised to a disulphide, although in the case in which barium peroxide was added to help this it had the effect of causing de-carboxylation, or the thiol may react with unchanged halogen compound to give a sulphide. The disulphides, furthermore, may decompose into mono- and tri-sulphides.

Replacement of Halogen by Selenium.—*o*-Bromobenzoic acid, neutralised by sodium hydroxide and heated with potassium selenocyanate and copper powder at 150°, gives diphenyl-diselenide-di-*o*-carboxylic acid, m. p. 296—297° (Lesser and Weiss, A., 1912, i, 643).

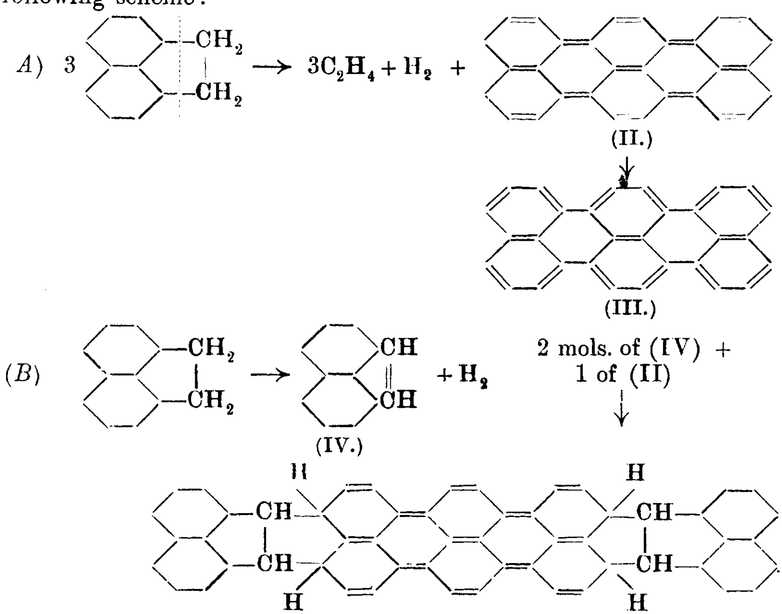
J. C. W.

Ethylenic Isomerism of the ω-Brominated Styrenes. CHARLES DUFRAISSE (*Compt. rend.*, 1921, **172**, 67—69. Compare this vol., i, 17).—It is shown that the two stereoisomeric ω-bromostyrenes (*loc. cit.*), having m. p.'s 7° and −7° respectively, are very sensitive to light. If freely exposed to light in separate tubes or mixed together in equal parts in a third tube, the contents of all three tubes rapidly reach a constant m. p. of +2°. It should be noted that in the case of the isomeride, m. p. 7°, the m. p. steadily falls to 2°, whereas with the isomeride, m. p. −7°, the m. p. first falls very gradually to −9°, then very suddenly to −20°, and then rises rapidly to +2°. Although the isomeride, m. p. 7°, is the more stable, it is the one which is the more sensitive to light. This effect of light explains the difficulties which some authors have had in preparing pure ω-bromostyrenes.

W. G.

The Bromine Compounds of Phenanthrene. I. HERBERT HENSTOCK (T., 1921, **119**, 55—61).

Three New Hydrocarbons, Leucacene, Rhodacene, and Chalkacene. KAROL DZIEWOŃSKI [with J. PODGÓRSKA, Z. LEMBERGER, and J. SUSZKA] (*Ber.*, 1920, **53**, [*B*], 2173—2192).—A modified and extended account of work published in *Bull. Acad. Sci. Cracow*, 1916, 159. When acenaphthene is distilled through a red-hot tube, the chief product is acenaphthylene (IV), but the distillate also contains a number of sparingly soluble, multi-nuclear hydrocarbons. Three of these, colourless leucacene (I), violet rhodacene (II), and bronze-red chalkacene (III), are now described, their relationships to each other and to acenaphthene being given in the following scheme:



(I.)

(*C*) When heated at above 200°, (I) ⟶ (II) ⟶ (III).

Leucacene (peri-*diacenaphthylenerhodacene*) (I) forms colourless platelets or silky needles, m. p. 250°, and crystallises from benzene as the *compound*, $4C_{54}H_{32},5C_6H_6$. When heated at 175° under reduced pressure it decomposes into acenaphthylene and rhodacene. It becomes pink on exposure to the air, gives striking colour changes when treated in chilled solutions with bromine or nitric acid, and yields naphthoic acid on oxidation with chromic acid.

Rhodacene (quinonoid-peri-*dinaphthylenenaphthalene*) (II) is best obtained by boiling a 4% solution of leucacene in nitrobenzene for about ten minutes, cooling the dark bluish-red liquid, filtering, concentrating the solution by distillation under reduced pressure,

and adding alcohol, when it is precipitated as a dark violet, microcrystalline powder, resembling methyl-violet. It has m. p. 338—340°, and its solutions in benzene hydrocarbons resemble those of the finest red phthaleins, exhibit brilliant red fluorescence, and have absorption bands at $\lambda = 575—555\ \mu\mu$, $535—510\ \mu\mu$, $495—475\ \mu\mu$, and $460—445\ \mu\mu$. When the solutions are exposed to bright light they soon become orange-yellow, and this is also the result of continuing the boiling of a solution of leucacene in nitrobenzene, isomerisation to the more stable chalkacene taking place.

Chalkacene (benzenoid-peri-*dinaphthylenenaphthalene*) (III) is found in the fractions of the distillate of acenaphthene which are least soluble in benzene, and may be extracted from this residue by boiling cumene. It is best obtained from leucacene as above, and separates from the fluorescent, bronzy solution in nitrobenzene as coppery-red, glistening, flat needles or tablets, m. p. 358—360°. The dilute solutions show absorption bands at $\lambda = 565—535\ \mu\mu$ and $525\ \mu\mu$ ultra-violet.

Other hydrocarbons may also be isolated by manipulation with various solvents, including "*polyacenaphthylene*," $C_{264}H_{176}$, a colourless powder, m. p. above 330°, and three "*chromacenes*," α-, dark red, m. p. 240°; β-, brownish-red, m. p. about 265°; and γ-, black, m. p. above 400°. These have yet to be investigated. J. C. W.

Abnormal Aniline Salts. HJ. MANDAL (*Ber.*, 1920, **53**, [*B*], 2216—2218).—When a solution of aniline hydrochloride in hot aniline is cooled, slender crystals of a *compound*, $2NH_2Ph,HCl$, are deposited, which part with the excess of base gradually at 18° or on solution in water. A *salt*, $7NH_2Ph,HBr$, may also be isolated.

J. C. W.

Methyl Dimethylaminobenzenesulphonates, and the Nitrosation of *N*-Methylanilinesulphonic Acids in the Nucleus. J. HOUBEN and G. SCHREIBER (*Ber.*, 1920, **53**, [*B*], 2346—2351).—When aniline-*o*-sulphonic acid is dissolved in sodium carbonate and shaken with methyl sulphate it yields o-*methylaminobenzenesulphonic acid*, decomp. 220°, but when boiled with methyl sulphate alone it gives *methyl* o-*dimethylaminobenzenesulphonate*, $NMe_2\cdot C_6H_4\cdot SO_3Me$, colourless needles. *Methyl* m-*dimethylaminobenzenesulphonate*, from metanilic acid, and *methyl* p-*dimethylaminobenzenesulphonate*, from sulphanilic acid, also crystallise well, but have no definite m. p. or decomposition point.

When carefully treated with powdered sodium nitrite in concentrated hydrochloric acid, *o*-methylaminobenzenesulphonic acid yields the yellow *hydrochloride* of 5-*nitroso-2-methylaminobenzenesulphonic acid*, which may be converted into metallic salts of the free acid. The *ammonium* salt forms dark bluish-green leaflets; the sodium and potassium salts are similar, and the barium salt crystallises in well-developed, pale green needles. When dissolved in sodium hydroxide, the ammonium salt immediately evolves methylamine, and the solution changes gradually from reddish-yellow to deep red. J. C. W.

2 : 4 : 6-Trinitrotolylmethylnitroamine. OSCAR LISLE BRADY and WILLIAM HOWIESON GIBSON (T., 1921, **119**, 98—104).

Chemical Constitution and Rotatory Power. V. Derivatives of α-Anisylethylamine [α-*p*-Methoxyphenylethylamine]. MARIO BETTI and ASSUNTA CAPACCIÒLI (*Gazzetta*, 1920, **50**, ii, 276—280).—The compounds formed by condensation of *d*-α-*p*-methoxyphenylethylamine (Betti and Del Rio, A., 1912, i, 347) with various aldehydes have been prepared and their rotatory powers measured in benzene solution at 18—20°. The *benzylidene* derivative forms a dense, yellow oil; the *salicylidene* derivative, $C_{16}H_{17}O_2N$, silky, yellow crystals, m p. 66°, $[\alpha]_D$ −139·76°; the 5-*bromosalicylidene* derivative, $C_{16}H_{16}O_2NBr$, pale yellow needles, m. p. 116—117°, $[\alpha]_D$ −34·73°; the p-*dimethylaminobenzylidene* derivative, $C_{18}H_{22}ON_2$, yellow needles, m. p. 105°, $[\alpha]_D$ −170·21°; the *vanillylidene* derivative, white needles, m. p. 130—131°, almost insoluble in benzene; the p-*hydroxybenzylidene* derivative, brown crystals, m. p. 162—163°; the 5-*nitrosalicylidene* derivative, yellow, shining needles, m. p. 106—107°, $[\alpha]_D$ −4·00°; the 3-nitrosalicylidene derivative, a brown resin. With the other aldehydes employed, *d*-α-*p*-methoxyphenylethylamine forms condensation products which are viscous and non-crystallisable.

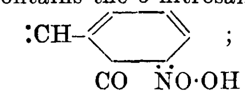
These results are in accord with those previously obtained (A., 1907, ii, 661, 726; A., 1916, ii, 279). As the acid character of the phenyl group of the aldehyde is gradually increased by the introduction of substituents, so the specific rotation of the condensation product formed with *d*-α-*p*-methoxyphenylethylamine becomes diminishingly negative in value. A compound containing a more acid residue than the 5-nitrosalicylidene residue would probably exhibit a positive rotation. T. H. P.

Chemical Constitution and Rotatory Power. Aldehydo-amino-derivatives of α-Aminophenyl-α-naphthylmethane. SERGIO BERLINGOZZI (*Gazzetta*, 1920, **50**, ii, 281—284).—Condensation products have been obtained by the interaction of *d*- and *l*-α-aminophenyl-α-naphthylamines (A., 1920, i, 480, 670) with various aldehydes. The optical rotations were measured in benzene solution at about 20°.

The p-*dimethylaminobenzylidene* derivative of the lævo-base, $C_{26}H_{24}N_2$, forms straw-yellow, shining scales, m. p. 198—199°, $[\alpha]_D$ +222·62°; the *anisylidene* derivative of the dextro-base, $C_{25}H_{21}ON$, tufts of white needles, m. p. 124—125°, $[\alpha]_D$ −180·92°; the *benzylidene* derivative of the dextro-base, $C_{24}H_{19}N$, minute, white prisms, m. p. 107—108°, $[\alpha]_D$ −162·94°; the p-*chlorobenzylidene* derivative of the lævo-base, $C_{24}H_{18}NCl$, a white, microcrystalline powder, m. p. 110—111°, $[\alpha]_D$ +138·97°; the o-*chlorobenzylidene* derivative of the lævo-base, shining, white scales, m. p. 124°, $[\alpha]_D$ +130·37°; the o-*nitrobenzylidene* derivative of the lævo-base, $C_{24}H_{18}O_2N_2$, lemon-yellow, shining needles or scales, m. p. 100—101°, $[\alpha]_D$ +72·13°; the 3-*nitrosalicylidene* derivative of the lævo-base,

$C_{24}H_{18}O_3N_2$, orange-yellow, silky needles, m. p. 157—158°, $[\alpha]_D$ +171·89°.

These results obtained are in full accord with those given by Betti and his collaborators (A., 1907, ii, 661, 726; preceding abstract) for the corresponding derivatives of α-aminophenyl-$\alpha\beta$-hydroxy-naphthylmethane, the molecular rotations being in the same order in the two series of derivatives. In each case an exception is furnished by the 3-nitrosalicylidene derivative, which is intensely yellow, and, according to Hantzsch, contains the *o*-nitrosalicylidene residue in the pseudo-phenolic form,



; thus, the salicylic hydroxyl is lacking, and the grouping :NO·OH occupies the meta-position, in which the electronegative influence is weakest (Betti, *loc. cit.*). T. H. P.

Preparation of Methyl Derivatives of the Xylidines and Naphthylamines by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1920, **171**, 1154—1155).—When the xylidines or naphthylamines in the form of vapour are passed along with methyl alcohol vapour over aluminium oxide at 360—380°, in all cases a mixture of mono- and di-methyl derivatives is obtained, the whole of the primary base being methylated. W. G.

Hypnotics. JOSÉ PUYAL and (MLLE) MONTAGNE (*Bull. Soc. chim.*, 1920, [iv], **27**, 857—862).—The authors have prepared a number of urethanes, in which either a chlorine atom or a phenyl group has been introduced, with a view to a study of their hypnotic properties. The urethanes of the type $CH_2Cl\cdot CH_2\cdot CHR\cdot O\cdot CO\cdot NH_2$ have been prepared from the chlorohydrins by the action of carbonyl chloride followed by that of ammonia. The alcohols corresponding with the urethanes of the type $CHPhR\cdot O\cdot CO\cdot NH_2$ were prepared either by reducing the corresponding ketones or by the action of benzaldehyde on the organo-magnesium compounds, or by the action of aldehydes on magnesium phenyl bromide. *Ethylchloroethylcarbinylurethane* has m. p. 68°; *chloroethylpropylcarbinylurethane*, m. p. 68°; *phenylmethylcarbinylurethane*, m. p. 78°; *phenylethylcarbinylurethane*, m. p. 89°; *phenylpropylcarbinylurethane*, m. p. 80°; *phenylbutylcarbinylurethane*, m. p. 75°; *ethylvinylcarbinylurethane*, m. p. 73°; *phenylvinylcarbinylurethane*, m. p. 146°; *γ-chloro-α-ethoxy*iso*propylurethane*, m. p. 50°, b. p. 175°/12 mm.; *α-phenoxy-γ-ethoxy*iso*propylurethane*, m. p. 72°; *chloroethylurethane*, m. p. 76°; and cyclo*hexylurethane*, m. p. 110°. W. G.

The Ketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Ann. Chim.*, 1920, [ix], **14**, 322—359).—A full account of work already published (compare A., 1913, i, 873; 1914, i, 830, 1075; 1919, i, 447; 1920, i, 442). W. G.

Tri-*o*-anisyltelluronium Salts. KARL LEDERER (*Ber.*, 1920, **53**, [*B*], 2342—2346).—These salts are obtained by the action of

magnesium *o*-anisyl bromide on tellurium tetrachloride, the crude product being conveniently purified in the form of the iodide. *Tri-o-anisyltelluronium iodide*, $Te(C_6H_4{\cdot}OMe)_3I$, forms long, asbestos-like fibres, m. p. 190° (turbid), 191—192° (clear), crystallises from water with $2H_2O$, m. p. 126—127°, and gives a *mercuri-iodide*, m. p. 234—235°. The *chloride*, obtained by boiling the iodide solution with silver chloride, crystallises in silky needles with $4H_2O$, m. p. 112°, or felted needles with 1EtOH, m. p. 114° (175—176° if slowly heated), and forms a *mercurichloride*, m. p. 244—245°. The *bromide*, m. p. 202—203°, obtained from the chloride by means of potassium bromide, crystallises in silky masses with $2H_2O$, m. p. 112°, or in flocculent masses with 1EtOH, and forms a *mercuri-bromide*, m. p. 218°. The *picrate* has m. p. 169—170°. J. C. W.

The Acid and Poly-acid Salts of Monobasic Acids; Monopotassium and Monolithium Dibenzoates. PHILIPPE LANDRIEU (*Compt. rend.*, 1920, **171**, 1066—1067).—Potassium gives a potassium dibenzoate, $C_6H_5{\cdot}CO_2K,C_6H_5{\cdot}CO_2H$, and lithium gives a *lithium dibenzoate*, $C_6H_5{\cdot}CO_2Li,C_6H_5{\cdot}CO_2H$. The curves representing the composition of the mother liquors are practically the same for the three alkali benzoates, although the only acid sodium salt existing at the ordinary temperature is the tribenzoate, whilst the only acid salts of potassium and lithium under the same conditions are the dibenzoates. W. G.

Sweetness of "Saccharin" and "Dulcin." THEODOR PAUL (*Chem. Zeit.*, 1921, **45**, 38).—The sweetness of "saccharin" is increased by the addition of "dulcin," which, by itself, has a lower sweetening property. For instance, a mixture of 280 mg. of "saccharin" and 120 mg. of "dulcin" dissolved in 1 litre of water has the same sweetness as 535 mg. of "saccharin" dissolved in 1 litre of water. W. P. S.

Formation of Derivatives of Tetrahydronaphthalene from γ-Phenyl Fatty Acids. GEORGE ARMAND ROBERT KON and ARNOLD STEVENSON (T., 1921, **119**, 87—94).

Nitrososalicylic Acid and Nitrosoanthranilic Acid. J. HOUBEN and G. SCHREIBER (*Ber.*, 1920, **53**, [*B*], 2352—2362).—*N*-Methylanthranilic acid is nitrosated by adding powdered sodium nitrite to a chilled solution in a mixture of pure sulphuric and acetic acids, 5-nitroso-2-methylaminobenzoic acid being deposited in the form of a yellow *hydrogen sulphate*,

$$CO_2H{\cdot}C_6H_3(\colon N{\cdot}OH)(\colon NMe),H_2SO_4.$$

Methyl 5-nitroso-2-methylaminobenzoate (A., 1909, i, 646) and the ethyl ester (*ibid.*) are obtained in better yields than before by shaking the *N*-methylanthranilates with sodium nitrite and concentrated hydrochloric acid in stoppered bottles. These esters are converted into the 5-*nitrososalicylates* by distillation in steam from their solutions in dilute sulphuric or phosphoric acid, the new esters condensing in the receiver; the *methyl* ester forms blue cubes or octahedra,

m. p. 89—90°, and the *ethyl* ester large, blue needles, m. p. 47—48°, whilst their ammonium salts are green and give reddish-brown solutions in water.

The nitrososalicylic acid and its esters are converted into the corresponding nitrosoanthranilates by melting with ammonium acetate (10 parts), chloride (5 parts), and carbonate (a trace). *Methyl 5-nitrosoanthranilate*, $NO\cdot C_6H_3(NH_2)\cdot CO_2Me$, crystallises from water in long, dark green needles, or sublimes as pale green needles, m. p. 167—168°; the *ethyl* ester forms small, green needles with violet-blue shimmer, m. p. 139°; whilst the free acid is a pure green substance which can only be kept as a *hydrochloride*,

$$NO\cdot C_6H_3(NH_2)\cdot CO_2H,HCl,H_2O,$$

pale yellow needles, or pale green *ammonium* salt. J. C. W.

The Fluorene Series. III. Derivatives of Ethyl Dibromofluoreneglyoxylate. ADOLF SIEGLITZ (*Ber.*, 1920, **53**, [*B*], 2241—2249. Compare A., 1920, i, 27, 605).—Ethyl 2:7-dibromofluorene-9-glyoxylate, obtained by the action of ethyl oxalate on 2:7-dibromofluorene in the presence of sodium ethoxide, forms an *oxime*, hard prisms, m. p. 226—228° (decomp.), and a *phenylhydrazone*, pale yellow needles, m. p. 182—183° (decomp.). The *methyl* ester crystallises in yellow needles, m. p. 153—154°, and yields a *benzoyl* derivative, canary-yellow needles, m. p. 174—175°, an *oxime*, felted needles, m. p. 209—210° (decomp.), and a *phenylhydrazone*, pale yellow needles, m. p. 188—189° (decomp.). The free *2:7-dibromofluorene-9-glyoxylic acid* (I) is obtained by warming the ester with 10% potassium hydroxide for a few minutes; it crystallises in thin, orange-yellow needles, m. p. 243° (decomp.), and forms a *phenylhydrazone*, slender, lemon-yellow needles, m. p. 211—212° (decomp.).

$$\begin{matrix}C_6H_3Br\\ |\\ C_6H_3Br\end{matrix}\!\!>CH\cdot CO\cdot CO_2H \qquad \begin{matrix}C_6H_3Br\\ |\\ C_6H_3Br\end{matrix}\!\!>CH\cdot CH(OH)\cdot CO_2H$$

(I.) (II.)

$$\begin{matrix}C_6H_3Br\\ |\\ C_6H_3Br\end{matrix}\!\!>C{:}CH\cdot CO_2H.$$

(III.)

The esters are reduced by means of amalgamated aluminium and water to esters of *2:7-dibromofluorene-9-glycollic acid* (II); the *methyl* ester forms colourless needles, m. p. 108°, and the *ethyl* ester nodules of rods, m. p. 119—120°. When boiled with potassium hydroxide, these esters give rise to *2:7-dibromodibenzofulvene-ω-carboxylic acid* (III), which crystallises in brilliant, deep orange needles, m. p. 263° (decomp.), and forms yellow esters (*methyl*, m. p. 152—153°; *ethyl*, m. p. 172—173°). The fulvene derivative is reduced by zinc dust and ammonia to *2:7-dibromofluorene-9-acetic acid*, stout prisms, m. p. 193—194°, the esters of which are also obtained by the action of aluminium amalgam on the fulvenoid esters (*methyl*, spikes, m. p. 122—123°; *ethyl*, rhombic leaflets, m. p. 94—95°).

The hydrogen atom in position 9 of the original ester is replaceable by sodium, and the compound reacts with a variety of halogen compounds in the usual way. By boiling the products with potassium hydroxide, 9-alkyl derivatives of 2:7-dibromofluorene are obtained. Thus, using ethyl bromoacetate, the above 2:7-dibromofluorene-9-acetic acid may be obtained, and from ethyl β-bromopropionate, β-2:7-*dibromofluorene-9-propionic acid*, which crystallises in rosettes of needles, m. p. 183—184°. In a similar manner may be prepared 2:7-*dibromo-9-methylfluorene*, glistening leaflets, m. p. 137—138°, 2:7-*dibromo-9-ethylfluorene*, m. p. 80—81°, and 2:7-*dibromo-9-benzylfluorene*, shimmering leaflets, m. p. 126—127°. It is much more convenient to prepare the last, however, by reducing 2:7-dibromo-9-benzylidenefluorene with aluminium amalgam in moist ether, and in this way 2:7-*dibromo-9-p-methylbenzylfluorene*, m. p. 141—142°, 2:7-*dibromo-9-o-chlorobenzylfluorene*, m. p. 117°, 2:7-*dibromo-9-p-chlorobenzylfluorene*, m. p. 150°, 2:7-*dibromo-9-p-methoxybenzylfluorene*, m. p. 144—145°, and 2:7-*dibromo-9-furfurylfluorene*, m. p. 110—111°, have been obtained.

Other products derived from the sodium salt of the dibromofluoreneglyoxylate are as follows. By means of ω-bromoacetophenone, 2:7-*dibromo-9-phenacylfluorene*, long, glistening needles, m. p. 183—184°; with α- and β-naphthylmethyl bromides, 2:7-*dibromo-9-α-naphthylmethylfluorene*, m. p. 167—168°, and 2:7-*dibromo-9-β-naphthylmethylfluorene*, m. p. 145—146°; with 9-bromofluorene, 2:7-*dibromo-9:9′-difluorenyl*, m. p. 269—270°; and with iodine, 2:2′:7:7′-tetrabromo-9:9′-difluorenyl, m. p. 317—318° (Schmidt, A., 1912, i, 179, gave m. p. 284°).

The red product described in the previous communication is 2:7:2′:7′-*tetrabromo-$\alpha\delta$-dibiphenylene-$\Delta^{\alpha\gamma}$-butadiene*,

$$\begin{matrix} C_6H_3Br \\ | \\ C_6H_3Br \end{matrix}\!\!>C{:}CH{\cdot}CH{:}C<\!\!\begin{matrix} C_6H_3Br \\ | \\ C_6H_3Br \end{matrix},$$

and has now been obtained in red needles, m. p. above 320°, by shaking a hot solution of dibromofluorene and sodium in alcohol with air for a few days. J. C. W.

Synthesis of γ-Coccinic Acid and Attempt to Synthesise Cochenillic Acid. C. A. Schleussner and H. Voswinckel (*Annalen*, 1921, **422**, 111—133).—Fritsch's method of introducing the carboxyl group into the nucleus of aromatic hydroxy-acids by means of chloral hydrate and sulphuric acid (A., 1897, i, 568) has hitherto always been applied to the methylated hydroxy-ester, and in no case has it been possible to eliminate the methyl from the methoxy-group in the product of the reaction. The authors now show that, under suitable conditions, the free hydroxy-acids can be utilised in the reaction. A solution of 5-hydroxy-*p*-toluic acid and chloral hydrate in concentrated sulphuric acid is poured into ice-water after two or three days, whereby are obtained a precipitate of 6-*hydroxy-4-methyl-2-trichloromethyl-*

phthalide, $OH\cdot C_6H_2Me<\begin{matrix}CH(CCl_3)\\CO\end{matrix}>O$, m. p. about 300°, and a solution of *ββ β-trichloro-α-5-hydroxy-4-carboxy-*m*-tolylethyl alcohol* [*6-hydroxy-4-methyl-2-tri-β-chloro-α-hydroxyethylbenzoic acid*], $CO_2H\cdot C_6H_2Me(OH)\cdot CH(OH)\cdot CCl_3$, needles with $1H_2O$, m. p. 208°. The former is converted into the latter by boiling water, and each is converted into the other by renewed treatment with chloral hydrate and sulphuric acid. By digesting the former with 10% sodium hydroxide at about 30°, or the latter with 5% sodium hydroxide at 50°, and then acidifying with hydrochloric acid, *3-hydroxy-2-carboxy-5-methylmandelic acid*,

$$CO_2H\cdot C_6H_2Me(OH)\cdot CH(OH)\cdot CO_2H,$$

faintly yellow needles, m. p. 204° (decomp.), is obtained (in the former case, 2 : *6-dihydroxy-4-methylphthalide*,

$$OH\cdot C_6H_2Me<\begin{matrix}CH(OH)\\CO\end{matrix}>O,$$

yellow, microscopic leaflets, m. p. 276° [decomp.], is obtained as a by-product), which is oxidised to *γ-coccinic acid* (*3-hydroxy-5-methylphthalic acid*), thin leaflets, m. p. 226—228° after sintering at about 215°, by alkaline 3% permanganate solution. γ-Coccinic acid develops an intense reddish-violet coloration with alcoholic ferric chloride, yields an *anhydride*, $C_9H_6O_4$, faintly yellow needles, m. p. 209°, an *acetyl* derivative, $C_{11}H_{10}O_6$, faintly yellow prisms, m. p. 196°, an *anhydride* of the acetyl derivative, $C_{11}H_8O_5$, leaflets, m. p. 200°, a *1-ethyl 2-hydrogen* ester, $C_{11}H_{12}O_5$, needles with $\frac{1}{2}H_2O$, m. p. 224° (decomp.), and a methyl ether, m. p. 202° (Meldrum, T., 1911, **99**, 1720, gives m. p. 200°). An attempt to synthesise cochenillic acid by treating γ-coccinic acid with chloral hydrate and concentrated sulphuric acid was unsuccessful, γ-coccinic acid being recovered mainly unchanged, and only 8% of a chlorine-containing product being obtained. C. S.

Bile Salts. VI. Contributions to the Decomposition of Deoxybilianic Acid. HEINRICH WIELAND and ALBERT KULENKAMPFF (*Zeitsch. physiol. Chem.*, 1920, **108**, 295—305. Compare A., 1916, i, 710; 1917, i, 685; 1919, i, 572, 576).—Deoxybilianic acid (cholanic acid), $C_{24}H_{36}O_7$, prepared by treating deoxycholic acid with fuming nitric acid, is separated from the *iso*-acid by extracting the latter with boiling alcohol; it has m. p. 293—295°, $[\alpha]_D^{22}$ +93·7° in alcohol. The ethyl ester gave m. p. 127—128°. The barium salt was also prepared. *iso*Deoxybilianic acid shows m. p. 247—248°. *Pyrodeoxybilianic acid*,

$$C_{23}H_{34}O_4,H_2O,$$

prepared by distilling deoxybilianic acid at 300° under diminished pressure, crystallises from alcohol in shining leaves, m. p. 197—198°, $[\alpha]_D^{22}$ +178·3° in absolute alcohol. It is a diketomonocarboxylic acid. The methyl ester with m. p. 147° was prepared. An *acid*, $C_{23}H_{34}O_6$, is obtained from the pyrodeoxybilianic acid by oxidising it with potassium permanganate. This acid crystallises from alcohol in branched, radiating leaves, m. p. about 216°, decomposing at 240°, $[\alpha]_D$ +181·35° in alcohol. It also is a diketo-

carboxylic acid. *Pyroisodeoxybilianic acid*, prepared by distilling *iso*deoxybilianic acid, crystallises in forms resembling those of pyrodeoxybilianic acid, m. p. 216—217°. The *barium* salt was obtained as slender needles. The oxidation of pyro*iso*deoxybilianic acid has not yielded any definite results. S. S. Z.

Bile Salts. VII. Choloidanic Acid. HEINRICH WIELAND (*Zeitsch. physiol. Chem.*, 1920, **108**, 306—330).—Choloidanic acid, $C_{24}H_{36}O_{10}$, prepared by treating deoxycholic acid with nitric acid (D 1·4), crystallises from glacial acetic acid in shining, broad needles, which sinter at 290°, evolves gas at 306°, and melts at 314°, $[\alpha]_D^{13}$ +40·19° in alcohol. From deoxybilianic acid, choloidanic acid is also obtained by treatment with nitric acid (D 1·4). Very pure cholic acid, on the other hand, does not yield choloidanic acid on oxidation with nitric acid. It is assumed that the choloidanic acid previously obtained by other investigators in this way was due to impurity of the cholic acid employed. The diethyl ester of choloidanic acid, $C_{28}H_{44}O_{10}$, was also prepared. The *pentamethyl* ester, $C_{29}H_{46}O_{10}$, was obtained by decomposing the silver salt with methyl iodide, and has m. p. 89—90°, and $[\alpha]_D^{13\cdot5}$ +50·5° in alcohol, +77·53—80·58° in benzene. *Pyrocholoidanic acid*, $C_{23}H_{32}O_6$, prepared by distilling choloidanic acid (as in the preparation of pyrodeoxybilianic acid, see preceding abstract), is dimorphic, and separates from glacial acetic acid either as voluminous, silky needles or as shining platelets. It melts at 222°, and has $[\alpha]_D^{13}$ +52·16° in alcohol. A *ketotricarboxylic acid*, $C_{23}H_{34}O_7$, obtained on boiling pyrocholoidanic acid with a small excess of $N/10$-alkali hydroxide, crystallises in voluminous needles, m. p. 263°. *ψ-Choloidanic acid*, $C_{22}H_{32}O_9$, obtained from the mother liquors in the preparation of choloidanic acid from deoxycholic acid, crystallises in long, silky needles, decomp. 301°, $[\alpha]_D^{14}$ +9·78° in alcohol. The *tetramethyl* ester, $C_{26}H_{40}O_9$, forms nodules, m. p. 132°. S. S. Z.

Oxidation of Anisaldoxime. Anisaldoxime Peroxide. PAUL ROBIN (*Compt. rend.*, 1920, **171**, 1150—1153).—Like benzaldoxime (compare A., 1919, i, 592), anisaldoxime is oxidised by iodine and sodium carbonate to give anisaldoxime peroxide. When this peroxide is further oxidised by the same oxidising agent, it gives *dianisenyloxyazoxime* (annexed formula), long, silky, colourless needles, m. p. 182°,

$$OMe\cdot C_6H_4\cdot C\!\left\langle\begin{matrix}N{-}{-}\\ O\underset{\underset{O}{\|}}{N}\end{matrix}\right\rangle\! C\cdot C_6H_4\cdot OMe$$

dianisenylazoxime, long, silky needles, m. p. 135°, anisaldehyde, anisonitrile, and anisic acid. When boiled with benzene, anisaldoxime peroxide is decomposed, giving anisaldoxime and dianisenyloxyazoxime. These then react to give anisaldehyde and dianisenylazoxime, and, at the same time, a portion of the oxyazoxime is hydrolysed, giving anisonitrile and anisic acid.

Piperonaldoxime gives results comparable with those from benzaldoxime and anisaldoxime. W. G.

The Catalytic Hydrogenation of Suberone. MARCEL GODCHOT (*Compt. rend.*, 1920, **171**, 1387—1389).—When suberone is acted on by hydrogen in the presence of reduced nickel at 175°, it is almost entirely converted into suberol. If the hydrogenation is carried out at 240°, suberol is obtained, along with some unchanged suberone, but there is no indication of any isomerism to a six-carbon ring compound, such as has been reported for *cyclo*heptane (compare Willstätter and Kametaka, A., 1908, i, 401). W. G.

The so-called true Dibenzoylmethane of J. Wislicenus. CHARLES DUFRAISSE (*Compt. rend.*, 1920, **171**, 1062—1065).—Wislicenus (A., 1900, i, 37) obtained a phenyl bromostyryl ketone, m. p. 44°, to which he assigned the constitution

CPhBr:CH·COPh.

By the addition of hydrogen bromide to benzoylphenylacetylene, the author obtains an isomeride, m. p. 42°. By the addition of bromine, these two isomerides give tribromo-compounds, having m. p.'s 103—104° and 98—99° respectively. It is shown, further, that the phenyl bromostyryl ketone, m. p. 44°, when heated with powdered sodium hydroxide, gives benzoic acid and ω-bromostyrene. The author considers that the constitution given by Wislicenus for his bromo-compound is incorrect, and that it should have the constitution CHPh:CBr·COPh, whilst the new isomeride has the constitution CPhBr:CH·COPh. As a result of this, the compound derived from phenyl bromostyryl ketone by Wislicenus, and described by him as dibenzoylmethane, is really benzoylphenylethylene oxide, $\begin{array}{l}\mathrm{COPh{\cdot}CH}\\ \quad\ \ |\\ \quad\mathrm{CHPh}\end{array}\!\!>\!\mathrm{O}$. W. G.

1 : 5-Dimethyl-1-dichloromethyl-Δ$^{3:5}$-*cyclo*hexadiene-2-one. K. VON AUWERS and K. ZIEGLER (*Ber.*, 1920, **53**, [*B*], 2299—2304).—A number of chlorinated hydroaromatic ketones of the *para*-series have been obtained by the action of chloroform on phenols in alkaline solution, but only one member of the *ortho*-series, namely, the product from *o*-cresol (A., 1903, i, 100). It is now shown that *as*-*m*-xylenol gives both types, which may be separated by fractional distillation under reduced pressure, the *ortho*-compound having the lower b. p. and remaining liquid. The yield is, however, very small. 1 : 5-*Dimethyl*-1-*dichloromethyl*-Δ$^{3:5}$-cyclo*hexadiene*-2-*one* (2-*keto*-1 : 5-*dimethyl*-1-*dichloromethyl*-1 : 2-*dihydrobenzene*) is a pale yellow oil, b. p. 125—125·5°/15 mm., $D_4^{19.8}$ 1·2250, n_α 1·52906, n_D 1·53366, n_β 1·54766, all at 19·8°. It does not react with semicarbazide or *p*-nitrophenylhydrazine, and magnesium phenyl iodide converts it into 1 : 4 : 5-*trimethyl*-1-*dichloromethyl*-Δ^5-cyclo*hexene*-2-*one*, which is a colourless oil with peppermint odour, b. p. 125—127°/13 mm., D_4^{20} 1·163, n_D^{20} 1·5080. This ketone is transformed in sulphuric acid solution, in the cold, into 1 : 4 : 5-*trimethyl*-1-*dichloromethyl*-Δ^3-cyclo*hexene*-2-*one*, b. p. 156—158°/7 mm., $D_4^{19.8}$ 1·1971, n_α 1·52013, n_D 1·52392, n_β 1·53417, n_γ 1·54298, all at 19·8°. J. C. W.

β-Amino-β-phenylpropiophenone. ALEX. MCKENZIE and FRED BARROW (T., 1921, **119**, 69—76).

Preparation of Bornyl Formate. A. LUTTRINGER and ANDRÉ DUBOSC (*Bull. soc. ind. Rouen*, 1920, **48**, 83—84).—Bornyl formate in 82% yield was obtained by heating at 112—114° for several hours 1 part of pinene hydrochloride with 2 parts of anhydrous sodium formate and 5 parts of 90% formic acid. The reaction does not go to completion. CHEMICAL ABSTRACTS.

The Action of Formic Acid on Dry Pinene Hydrochloride. A. LUTTRINGER and ANDRÉ DUBOSC (*Bull. soc. ind. Rouen*, 1920, **48**, 84).—About 14% of esters were formed by using a large excess of 90% formic acid and heating for eight hours.

CHEMICAL ABSTRACTS.

Preparation of Bornyl Formate by the Action of Sodium Formate and Powdered Zinc on Solid Pinene Hydrochloride in the Presence of an Excess of Formic Acid. ANDRÉ DUBOSC and A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 85—86).—A mixture of pinene hydrochloride (6 parts), formic acid (90%; 250 parts), zinc powder (15 parts), and dried sodium formate (30 parts), after twenty hours' heating, yielded an ester practically free from chlorine and containing 68% of bornyl formate, the remainder being camphene and terpenes.

CHEMICAL ABSTRACTS.

Preparation of Bornyl Formate by the Action of Sodium Formate and Iron Filings on Solid Pinene Hydrochloride in the Presence of an Excess of Formic Acid. ANDRÉ DUBOSC and A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 86—87).—The same procedure as that of the preceding abstract, except that iron filings are used in place of zinc.

CHEMICAL ABSTRACTS.

Preparation of Bornyl Esters and subsequently of Camphor from Oil of Turpentine, Propionic Acid, and an Alkaline Peroxide. ANDRÉ DUBOSC and A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 87).—Oil of turpentine is heated with propionic acid or one of its homologues, or a mixture of several of the lower fatty acids, until an ester is formed. This is treated with a mixture of sodium peroxide and silicate and a small amount of water, whereby camphor is formed. CHEMICAL ABSTRACTS.

Preparation of the Bornyl Esters of Propionic, Butyric, and Valeric Acids. ANDRÉ DUBOSC and A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 88).—The procedure is the same as in the two preceding abstracts, except that propionic, butyric, or valeric acid is used instead of formic, and the corresponding sodium salt instead of sodium formate. Zinc is used.

CHEMICAL ABSTRACTS.

Preparation of Terpinyl Esters. A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 89).—A mixture of hydrogen, an oxide of carbon, steam, and the vapour of a terpene (for example, pinene or camphene) is passed through a heated tube containing a mixture of a metallic chloride (for example, chloride of copper, aluminium, zinc, or nickel) and reduced metal. Among the products formed are bornyl and terpinyl formates.

CHEMICAL ABSTRACTS.

The Preparation of Camphor from Oil of Turpentine by means of Salicylic Acid and an Alkaline Peroxide. A. DUBOSC and A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 85).—The oil is converted into an ester by dry salicylic acid or one of its homologues. The ester is heated with the peroxide of an alkali or an alkaline earth, forming camphor and a salicylate of the metal. CHEMICAL ABSTRACTS.

Synthetic Camphor. A. LUTTRINGER (*Bull. soc. ind. Rouen*, 1920, **48**, 90—91).—Some pine-needle oils, and also Siberian oil of turpentine, contain 30—45% of bornyl acetate, the remainder being terpenes. From 60% to 80% of the terpenes can be converted into bornyl formate by means of formic acid and a dehydrating agent. The mixture of bornyl esters can then be converted into a camphor which is free from compounds of chlorine. CHEMICAL ABSTRACTS.

Thermal Decomposition of Turpentine, with Particular Reference to the Production of Toluene and Isoprene. S. A. MAHOOD (*J. Ind. Eng. Chem.*, 1920, **12**, 1152—1155).—Although turpentine is a possible source of toluene, it does not give a sufficiently large yield of either toluene or isoprene to make it a practical source of these products. W. P. S.

Action of Concentrated Sulphuric Acid on Natural and Artificial Varieties of Caoutchouc. F. KIRCHHOF (*Kolloid Zeitsch.*, 1920, **27**, 311—315).—The action of cold concentrated sulphuric acid on raw caoutchouc, benzene solutions of raw caoutchouc and guttapercha, and benzene solutions of dimethylcaoutchouc (artificial), and the simultaneous action of phenol and sulphuric acid on artificial caoutchouc, have been investigated. Solid natural caoutchouc becomes at once hard and brittle under this treatment, but after a few days it again becomes soft, whilst there is a continuous evolution of sulphur dioxide. On treating the product with water, it again becomes hard and brittle. The action of sulphuric acid in the other cases is to produce white oxidation products. The exact nature of the products depends on (i) the nature of the solvent, (ii) the quantity and, particularly, the duration of the action of sulphuric acid, and (iii) the concentration and the nature of the caoutchouc. J. F. S.

Urson and its Distribution in the Plant World. A. M. NOOYEN (*Pharm. Weekblad*, 1920, **57**, 1128—1142).—Urson, an indifferent vegetable substance, was discovered in the leaves of *Arbutus Uva-ursi* by Trommsdorff; it is now shown to be a general constituent of the *Ericaceae* and of some *Ilex*. Urson forms white, crystalline needles, m. p. 273°. The formula $C_{10}H_{16}O$ given by Gintl, and also by van Itallie, is confirmed. Attempts to determine the molecular weight by the ebullioscopic and cryoscopic methods were unsuccessful, but from results obtained with the methyl ester and by titration of urson, the molecular weight of urson itself is deduced as 456, corresponding with the formula $(C_{10}H_{16}O)_3$. The methyl ester was found both by saponification and by Zeisel's method to contain only one methyl group.

The *potassium* and *sodium* salts form white needles, readily soluble in alcohol. The lead and silver salts could only be obtained in the amorphous condition. The substance and its salts are optically active, the potassium salt having $[\alpha]_D^{15}+58°$. Although Gintl, and also Dodge, described acetyl and benzoyl derivatives, all attempts to obtain these compounds failed; hydroxyl groups are thus absent, and aldehyde, ketone, or methoxyl groups could not be identified. The *methyl* ester forms white needles, m. p. 148°. No additive products with the halogens or ozone could be obtained either from the compound or its methyl ester, and hydrogen has no action. Oxidation with permanganate or chromic acid led to no definite results. With nitric acid, a *nitro*-compound, m. p. 210°, was obtained. The formula $C_{29}H_{47}O{\cdot}CO_2H,2H_2O$ is assigned to urson. S. I. L.

The Tannin of Oak Bark. K. FEIST and RICHARD SCHÖN (*Arch. Pharm.*, 1920, **258**, 317—318).—The tannin has been extracted from oak bark in a purer form than hitherto by applying a process previously described (Feist and Haun, A., 1914, i, 195). Contrary to earlier statements (Etti, A., 1883, 994), it contains no methoxyl group, and the methoxy-compounds associated with it have no tanning properties. By means of diazomethane, a stable methyl derivative was obtained, and found to have $[\alpha]_D^{15}$ $-43°$, and a molecular weight of about 1800. No compound could be found in the bark from which the tannin might be produced, but a preparation of catechin (which gives the same degradation products as the tannin in question) was also found to be lævorotatory. J. K.

β-2-Furylethylamine and β-Tetrahydro-2-furylethylamine. A. WINDAUS and O. DALMER (*Ber.*, 1920, **53**, [*B*], 2304—2308).—The authors have synthesised these bases by Curtius's azide method, hoping thereby to obtain physiologically active substances as an outlet for furfuraldehyde.

Ethyl β-2-furylpropionate is obtained as a limpid liquid of fruity odour, b. p. 209°/760 mm., by the action of alcoholic sulphuric acid (5%; not hydrochloric acid) on the well-known acid, and converted

into the *hydrazide*, m. p. 68—72°, which forms an *anisylidene* compound, $C_4H_3O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OMe$, long needles, m. p. 103°. The hydrazide is treated with sodium nitrite and sulphuric acid, the ethereal extract of the azide is dried, mixed with dry methyl alcohol, boiled, and the urethane left on evaporation is distilled with lime. *β-2-Furylethylamine*, $C_4H_3O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, is thus obtained as a pale yellow liquid, b. p. 159°, which absorbs carbon dioxide rapidly, forming a well-defined *carbamate*, $(C_6H_9ON)_2CO_2$, m. p. 84°. The base also yields a *benzoyl* derivative, long, white needles, m. p. 81°, and a *picrolonate*, yellow leaflets and prisms, m. p. 204° (decomp.).

β-2-Furylacrylic acid is hydrogenated in the presence of spongy palladium and converted into *β-tetrahydro-2-furylpropionic acid*, which is a colourless, viscous liquid, b. p. 263°/760 mm. The *ethyl* ester, b. p. 221°/750 mm., is prepared as above or by hydrogenating ethyl furylacrylate (Claisen, A., 1891, 427), and is converted ultimately into *β-tetrahydro-2-furylethylamine*, b. p. 173°/754 mm. This forms a *carbamate*, $(C_6H_{13}ON)_2CO_2$, m. p. 76°, a *picrate*, orange-yellow needles, m. p. 129°, and a *picrolonate*, orange-yellow needles, m. p. 175°.

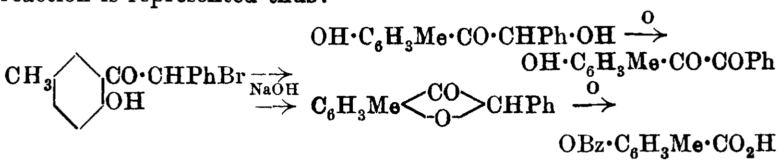
Injected into the jugular vein of a cat, furylethylamine causes an immediate but transient lowering of the blood pressure without influencing the pulse or respiration, in a dose of 0·0025 gram, but tetrahydrofurylethylamine is inactive in twice this dose. Comparing their behaviour on the isolated guinea-pig's uterus, furylethylamine is about one-quarter, and tetrahydrofurylethylamine about one-half, as active as hydrastinine. J. C. W.

Formation and Autoxidation of Coumaranones. K. von Auwers (*Ber.*, 1920, **53**, [*B*], 2271—2285).—In a number of cases it has been shown that the opening and closing of the oxygen-ring in coumaranones is dependent on the number and position of the substituents, compounds of the type $C_6H_4{<}{}^{CO}_{O}{>}CHR$, where R=alkyl, having a ring system which is easily ruptured by ketone reagents or through autoxidation (A., 1919, i, 217). Attempts have now been made to study the effect of the nature of the substituent, by synthesising coumaranones of the above type, in which R shall be phenyl, and it has been found that the aromatic nucleus is much more antagonistic to the stability of the ring than even the aliphatic radicle.

Phenylacetyl chloride and *p*-methoxytoluene are condensed by means of aluminium chloride in carbon disulphide; the solvent is removed, and the product is heated with another portion of aluminium chloride and decomposed by ice and hydrochloric acid, when 2-*hydroxy*-5-*methyldeoxybenzoin* [4-*hydroxy*-m-*tolyl benzyl ketone*], $OH{\cdot}C_6H_3Me{\cdot}CO{\cdot}CH_2Ph$, is obtained in stout, glassy needles, m. p. 65°, b. p. 214°/18 mm. (*semicarbazone*, m. p. 204—205°; p-*nitrophenylhydrazone*, m. p. 203—204°). The *acetate* of this also forms

stout, glassy needles, m. p. 73—74°, and yields a *bromo*-derivative, silky needles, m. p. 118—119°, when treated with bromine in carbon disulphide. The bromide is hydrolysed by boiling with hydrogen bromide dissolved in glacial acetic acid, and *α-bromo-2-hydroxy-5-methyldeoxybenzoin* [*4-hydroxy-*m*-tolyl α-bromobenzyl ketone*] is obtained in pale yellow, quadratic leaflets, m. p. 106°. Attempts to eliminate hydrogen bromide from this and thus effect ring closure gave unexpected results which are reviewed in the following paragraph.

When a solution in cold sodium hydroxide is acidified, a flocculent mass is deposited, which is presumably a mixture of 2-hydroxy-5-methylbenzoin and the desired 2-phenyl-5-methylcoumaran-3-one, but when this mass is exposed to the air it gradually becomes viscous, then oily, and finally solid. It now consists of *4-benzoyloxy-*m*-toluic acid*, which is sparingly soluble in heavy petroleum and forms a silvery, felted mass, m. p. 155—156°, and more freely soluble *2-hydroxy-5-methylbenzil*, yellow prisms, m. p. 90—91°. The reaction is represented thus:



The benzil derivative yields a *disemicarbazone*, m. p. 193—194°, a *di-*p*-nitrophenylhydrazone*, which changes at 225—240° from dark red to yellow and has m. p. 280—282°, and a methyl ether, *2-methoxy-5-methylbenzil*, stout needles, m. p. 106—106·5°. Elimination of bromine by means of sodium acetate gives conflicting results, but the only definite products are 4-benzoyloxy-*m*-toluic acid, and a *substance*, $C_{30}H_{24}O_4$, m. p. 227—232°, which has twice the molecular weight of the desired coumaranone. The product obtained by boiling with diethylaniline was expected to be the coumaranone, and was tested with ketone reagents, but it proved to be 4-hydroxy-*m*-tolyl benzyl ketone, the net result being replacement of bromine by hydrogen.

The proof of the constitution of the benzil derivatives is as follows. *2-Methoxy-5-methyldeoxybenzoin* [*4-methoxy-*m*-tolyl benzyl ketone*], b. p. 205—207°/14 mm., m. p. 75°, is obtained by condensing phenylacetyl chloride with *p*-methoxytoluene, or by the action of methyl iodide on the hydroxy-derivative, and treated with amyl nitrite, when the *β-oxime* of 2-methoxy-5-methylbenzil is formed in bundles of needles, m. p. 143—144°. This is hydrolysed by boiling with 20% sulphuric acid, giving 2-methoxy-5-methylbenzil, identical with the above. Characteristic derivatives of this diketone are prepared as follows: *di-oxime*, silky needles, m. p. 225—227°, from the *β*-oxime and hydroxylamine hydrochloride; *disemicarbazone*, m. p. 250—251°, from the diketone; *di-*p*-nitrophenylhydrazone*, brick-red, flat needles, m. p. 224·5—225·5°, from the diketone or the *β*-oxime. J. C. W.

3-Oxythionaphthens [2-Keto-1 : 2-dihydrothionaphthens]. K. VON AUWERS and W. THIES (*Ber.*, 1920, **53**, [*B*], 2285—2299).—A comparison has been made between coumaranones (I), hydrindones (II), and 2-keto-1 : 2-dihydrothionaphthens (III):

$$C_6H_4{<}{\scriptstyle CO \atop O}{>}CH_2 \qquad C_6H_4{<}{\scriptstyle CO \atop CH_2}{>}CH_2 \qquad C_6H_4{<}{\scriptstyle CO \atop S}{>}CH_2$$

(I.) (II.) (III.)

In the solid state the three groups are ketones, but the ketodihydrothionaphthens and coumaranones may react, even in the free state, as enols. Like the hydrindones and unlike the coumaranones, however, the ketodihydrothionaphthens do not, as far as can be ascertained, suffer rupture of the 5-ring when treated with semicarbazide or *p*-nitrophenylhydrazine. All three types undergo condensation, if the methylene group adjacent to the carbonyl is intact, giving compounds of the formula (IV). On the other hand, if

$$R{<}{\scriptstyle CO \atop CH_2(O,S)}{>}C{:}C{<}{\scriptstyle CH_2 \atop R}{>}CH_2(O,S) \qquad R{<}{\scriptstyle CO \atop S}{>}CPh{\cdot}CPh{<}{\scriptstyle CO \atop S}{>}R.$$

(IV.) (V.)

2-keto-1-phenyl-1 : 2-dihydrothionaphthen may be regarded as typical, the 1-alkyl or -aryl derivatives behave differently on autoxidation, the rings being opened in the case of coumaranones and hydrindones, but not in the case of the oxythionaphthens, which give compounds of the type (V).

2-Ketodihydrothionaphthen reacts with acetyl chloride to form 2-*acetoxythionaphthen*, $C_6H_4{<}{\scriptstyle C(OAc) \atop S}{>}CH$, a pale yellow oil, b. p. 165°/18 mm., $D_4^{20 \cdot 4}$ 1·2580, n_α 1·59718, n_D 1·60464, n_β 1·62328, at 20·4°, which suffers oxidation on exposure to the air to a pale reddish-yellow *compound*, $C_{20}H_{14}O_4S_2$, long, glistening needles, m. p. 164—165°. This compound was once obtained by heating *o*-carboxyphenylthiolacetic acid with acetic anhydride for an hour and leaving the mixture for forty hours. 2-Ketodihydrothionaphthen also yields a *semicarbazone*, pink needles, m. p. 224—226°, and a p-*nitrophenylhydrazone*, three forms of which are mentioned, a reddish-brown powder, m. p. 185—190°, a more red preparation, m. p. 205°, and a brownish-red, granular mass, m. p. 251—261°.

2-Keto-5-methyldihydrothionaphthen is prepared by the alkaline fusion of 4-carboxy-*m*-tolylthiolacetic acid (A., 1909, i, 251). It forms snow-white needles, m. p. 86—87°, and yields an *acetyl* derivative, golden-yellow, viscous oil, b. p. 168·5°/13 mm., a *semicarbazone*, pink needles, m. p. 232—233°, and a p-*nitrophenylhydrazone*, a reddish-brown powder, m. p. 222—227°, 245—252° (two preparations).

5-*Bromo*-2-*keto*-3-*methyl*-1 : 2-*dihydrothionaphthen* is prepared by warming 5-bromo-*m*-tolylthiolacetic acid with thionyl chloride and heating the product with aluminium chloride and carbon disul-

phide. It crystallises in long, thin needles, m. p. 134—135°, and behaves as a mono-ketone.

4-*Chloro-2-keto*-1 : 2-*dihydrothionaphthen*, m. p. 100°, is obtained by heating ethyl *p*-chlorophenylthiolacetate with phosphoric oxide (A., 1910, i, 764). The *semicarbazone* is a pink powder, m. p. 253°, and the p-*nitrophenylhydrazone* a reddish-brown powder, m. p. 270°.

When boiled with acetic anhydride, 4-chloro-3-ethoxyphenylthiolacetic acid forms 4-*chloro*-2-*acetoxy*-5-*ethoxythionaphthen*, snowy needles, m. p. 128—129°, which may be hydrolysed to 4-*chloro*-2-*keto*-5-*ethoxy*-1 : 2-*dihydrothionaphthen*. This crystallises in pale pink needles, m. p. 135·5—136·5°, and forms a *semicarbazone*, m. p. 250°, and p-*nitrophenylhydrazone*, m. p. 249—252°.

Attempts to prepare derivatives of 2-keto-1-methyl-1 : 2-dihydrothionaphthen were not very successful. Thus, α-p-*tolylthiolpropionic acid*, $C_6H_4Me\cdot S\cdot CHMe\cdot CO_2H$, stout crystals, m. p. 77·5—78·5°, from *p*-thiocresol, α-bromopropionic acid, and sodium hydroxide, was treated with thionyl chloride and then aluminium chloride, but gave only a small yield of what might be 2-keto-1 : 4-dimethyl-1 : 2-dihydrothionaphthen (m. p. 117°). Similarly, *s*-*m*-thioxylenol was methylated and the s-m-*xylyl methyl sulphide*, b. p. 127°/24 mm., was heated with α-bromopropionyl bromide and aluminium chloride, but the oily product would not react with semicarbazide or *p*-nitrophenylhydrazine. Finally, 5-bromo-*m*-tolyl mercaptan was converted by condensation with α-bromopropionic acid into α-5-*bromo*-m-*tolylthiolpropionic acid*, large crystals, m. p. 78—79°, and this was treated with thionyl chloride and aluminium chloride. A brown oil was isolated which resinified most readily, but gave a semicarbazone, m. p. 236—237°, and a *p*-nitrophenylhydrazone.

2-Keto-1-phenyldihydrothionaphthen (A., 1914, i, 77) and 3-keto-1-*p*-nitrophenyldihydrothionaphthen (A., 1913, i, 1341) have already been described, and the data are now confirmed. J. C. W.

Angostura Alkaloids. J. TROEGER and K. BÖNICKE (*Arch. Pharm.*, 1920, **258**, 250—277).—Of the angostura alkaloids, the existence of galipidine and casparidine has not been confirmed by Troêger and Kroseberg (A., 1912, i, 895). An examination of the sample of the former base prepared by Beckurts and Frerichs (A., 1906, i, 34) has now shown that it gives an oxalate identical with that of galipine. *Galipine hydriodide*, $C_{20}H_{21}O_3N,HI$, yellow crystals, m. p. 178°, was also obtained from "galipidine." By analysis of this salt, and of known derivatives, the formula $C_{20}H_{21}O_3N$ originally attributed to galipine is confirmed (compare Troeger and Kroseberg, *loc. cit.*). From nitrogalipine the *hydrobromide*, $C_{20}H_{20}O_5N_2,HBr,2H_2O$ (yellow needles, m. p. 177°, which become anhydrous at 100°), the *hydriodide*, $C_{20}H_{20}O_5N_2,HI,3H_2O$ (yellow needles, m. p. 182°), and the *methiodide*, $C_{20}H_{20}O_5N_2,MeI$, m. p. 170°, were prepared. Demethylation of the nitro-compound by dry hydrogen chloride (compare Troeger and Müller, A., 1915, i, 447)

leads to a product which is difficult to purify, but by this treatment at a temperature not exceeding 190°, galipine is converted into the *phenol*, $C_{17}H_{15}O_3N$, m. p. 225° (*hydrochloride*,

$$C_{17}H_{15}O_3N,HCl,1\tfrac{1}{2}H_2O,$$

yellow prisms, m. p. 112°; *hydrobromide*,

$$C_{17}H_{15}O_3N,HBr,H_2O,$$

yellow prisms, m. p. 85°). Galipine further resembles cusparine in that it is isomerised when gradually heated in a stream of methyl iodide vapour from 130° to 190—200°. iso*Galipine*, $C_{20}H_{21}O_3N$, silky needles, m. p. 165°, contains two methoxyl groups and one methylimino-group. The *hydrochloride*,

$$C_{20}H_{21}O_3N,HCl,5H_2O,$$

plates, m. p. 234°; *hydrobromide*, $C_{20}H_{21}O_3N,HBr,H_2O$, yellow prisms, m. p. 223°; *hydriodide*, $C_{20}H_{21}O_3N,HI,H_2O$, yellow prisms, m. p. 206°; *platinichloride*, $(C_{20}H_{21}O_3N)_2,H_2PtCl_6,4H_2O$, dark yellow prisms, m. p. 198—199° (decomp.); the methiodide seems to be very unstable, and so does not lend itself to degradation by exhaustive methylation. *Nitro*iso*galipine*, $C_{20}H_{20}O_5N_2$, yellowish-brown needles, m. p. 237°, has very slight basic properties, but gives a *hydriodide*, $C_{20}H_{20}O_5N_2,HI,H_2O$, light yellow needles, m. p. 167—172°. The analogous behaviour of galipine and cusparine is considered to favour the identity of the acid, m. p. 262—264°, obtained by the oxidation of galipine (Troeger and Müller, A., 1910, i, 414) with the acid, m. p. 271—272°, from cusparine (Troeger and Beck, A., 1913, i, 748). If this be so, it follows that cusparine, like galipine (Troeger and Kroseberg), is also derived from 6-methoxyquinoline. The products of decomposition of galipine sulphate (Körner and Böhringer, A., 1884, 331) consist of more or less completely demethylated derivatives. The conditions for the formation of galipine methiodide are at present not at all clear, a circumstance which has so far prevented definite results from being obtained by exhaustive methylation. J. K.

Complete Synthesis of *r*-Ecgonine and of Tropinone. RICHARD WILLSTÄTTER and MAX BOMMER (*Annalen*, 1921, **422**, 15—35).—Willstätter's synthesis of tropine from suberone in 1902 was only of constitutional significance, being a reversal of the degradation to the *cyclo*heptane derivative. The authors have now synthesised *r*-ecgonine and tropinone from citric acid in a few steps, the important intermediary being ethyl succinyldiacetate (Willstätter and Pfannenstiel, this vol., i, 91). This ester reacts with warm ammonium acetate to give *ethyl pyrrole*-2:5-*diacetate*, $\begin{matrix}CH{:}C(CH_2{\cdot}CO_2Et)\\ |\\ CH{:}C(CH_2{\cdot}CO_2Et)\end{matrix}\!\!>\!NH$, domed prisms, m. p. 74—75°. Ethyl 1-methylpyrrole-2:5-diacetate (Willstätter and Pfannenstiel, *loc. cit.*; the *methyl* ester, prisms, has m. p. 170—171°) readily yields the corresponding *acid*, $C_9H_{11}O_4N$, rhombic plates, m. p. 150° (decomp.), by hydrolysis with boiling 10% methyl-alcoholic potassium hydroxide, and is reduced by Willstätter and Jacquet's method (A., 1918, i, 391) by hydrogen and platinum-black con-

taining oxygen in acetic acid suspension to *ethyl* 1-*methylpyrrolidine*-2 : 5-*diacetate*, $C_{13}H_{23}O_4N$, b. p. 162·5°/9 mm. (the *methyl* ester has b. p. 155·5°/12 mm.). This ester, which is probably a mixture of the *cis*- and the *cis-trans*-isomerides, of which only the former is suitable for further ring-closure, is diluted with cymene and heated with sodium powder at 172° for ten minutes, whereby ethyl tropinonecarboxylate is obtained in 25% yield. The latter is converted by boiling 10% sulphuric acid into tropinone (the identity of which with the product from natural tropine is well established, particularly by a comparison of the physical and crystallographic constants of the characteristic dibenzylidene derivative), and by reduction with sodium amalgam into *r*-ψ-ecgonine ethyl ester. The latter is converted by hydrolysis and subsequent esterification into the methyl ester, which is completely identical with the *r*-ψ-ecgonine methyl ester obtained by Willstätter and Bode (A., 1903, i, 361), and by benzoylation with benzoic anhydride in boiling toluene yields *d*-ψ-cocaine (*r*-cocaine) (Willstätter and Bode, *loc. cit.*).

Ethyl 1-methylpyrrolidine-2 : 5-diacetate resembles its next lower homologue, ethyl tropate, in its behaviour during exhaustive methylation; the *methiodide*, $C_{14}H_{26}O_4NI$, plates, m. p. 78°, is converted by warming with concentrated potassium carbonate solution at 60° for a few minutes into the de-methyl derivative,

$$CO_2Et{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CH_2{\cdot}CO_2Et,$$

which, by further treatment with methyl iodide and subsequently with boiling sodium hydroxide solution, yields trimethylamine and an unsaturated *acid*, needles, m. p. 260° (not sharp), which is probably $\Delta^{\beta\epsilon}$-*hexadiene*-$\alpha\zeta$-*dicarboxylic acid*,

$$CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H.$$

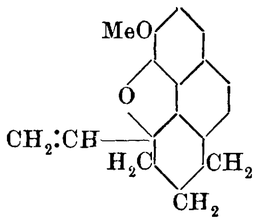
The spatial relationships of members of the tropan group are fully discussed. Ecgonine and cocaine can each exist in four *d*- and four *l*-forms, from which four racemates can be obtained. *l*-Ecgonine and *d*-ecgonine are not optical antipodes; they correspond with tropine and ψ-tropine, and are therefore designated *l*-ecgonine and *d*-ψ-ecgonine, the synthetic compound described above being *r*-ψ ecgonine. Corresponding with this difference in structure is the difference in the behaviour of their methiodides towards sodium hydroxide. It is well known that the methiodide of ordinary ecgonine (*l*-ecgonine) ester is very easily decomposed into dimethylamine and *cyclo*heptatrienecarboxylic acid by boiling for one minute with 10% sodium hydroxide solution. The methiodides of *d*-ψ-ecgonine and *r*-ψ-ecgonine esters do not yield dimethylamine under these conditions, and the decomposition is incomplete, even after prolonged boiling with 25% sodium hydroxide solution. C. S.

Influence of their Reaction on the Permanence of Cocaine Solutions. ALBERT RIPPEL (*Arch. Pharm.*, 1920, **258**, 287—295). —Hydrolysis of cocaine by acids or alkalis occurs very easily, and is accompanied by a diminution of physiological activity (Stockman, *J. Anat. Physiol.*, 1888, **21**, 46), which is also observed in

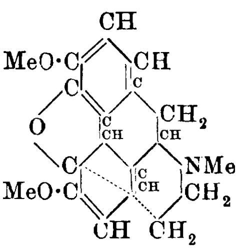
aqueous solutions when they are sterilised by heat. The activity of such solutions has now been measured by a comparison of them with solutions of known strength in the effect produced by their addition to a Ringer's solution supplied to a frog's heart. Boiling for one hour in neutral solution, or in a solution of the same alkalinity as the blood, produced diminutions in activity of 60—70% and 80% respectively, but no deterioration occurred in solutions varying in acidity from p_H 1 to p_H 5·8. Similar, but less rapid, changes occurred at the ordinary temperature. J. K.

Two New Reduction Products of Codeine. C. MANNICH and HELENE LÖWENHEIM (*Arch. Pharm.*, 1920, **258**, 295—316). —The difficulties encountered in the investigation of morphine and codeine, due to rearrangement into *apo*morphine, migration of the hydroxyl group (Knorr, A., 1907, i, 151), or the elimination of carbon atoms, along with nitrogen, by exhaustive methylation, are all connected with the partly reduced benzene nucleus. The authors have therefore sought a means of so modifying this nucleus by well-defined processes as to obviate the occurrence of the anomalous behaviour referred to, and so permit the application of the usual methods for determining constitution. Dihydrocodeine (Skita and Franck, A., 1911, i, 1017) may be obtained in three forms: a *dihydrate*, $C_{18}H_{23}O_3N,2H_2O$, which separates from alcohol in large plates, m. p. 55°, and is converted above its melting point into a second *dihydrate*, m. p. 87—88°; the anhydrous compound melts at 111—112°. It is unchanged by distillation with formic acid, but with hydriodic acid gives dihydromorphine, m. p. 156—158°. Chlorodihydrocodide (Freund, A., 1920, i, 758), m. p. 172—174°, gives a hydrochloride, m. p. 203°, and a *methiodide*, $C_{19}H_{25}O_2NClI$, needles, m. p. 244°, and is converted by hydriodic acid into *chlorodihydromorphide*, $C_{17}H_{20}O_2NCl$, prisms, m. p. 233°, which is apparently dimorphous. The chlorine atom in these compounds is very inert, and could not be replaced by hydrogen. Freund's results from the reduction of α-chlorocodide (*loc. cit.*) were confirmed, but, in addition, small quantities of the products of reduction of β-chlorocodide were observed. The latter compound, in presence of palladium, gave rise to a mixture, in which *dehydroxydihydrocodeine*, $C_{18}H_{23}O_2N$, m. p. 107°, $[\alpha]_D$ −81·47°, predominated. It contains one methoxyl group, and gives a yellow *picrate*, m. p. 207°, but no acetyl derivative. In it, therefore, the object of the investigation, as above described, is attained, since the hydroxyl group of codeine is replaced by hydrogen, and the benzene nucleus in question reduced. Correspondingly, its *methiodide*, $C_{19}H_{26}O_2NI$, prisms, m. p. 256—257°, behaves normally towards potassium hydroxide, and gives *dehydroxydihydrocodomethine*, $C_{19}H_{25}O_2N$, m. p. 86° (*picrate*, m. p. 154°; *hydrochloride*, $C_{19}H_{25}O_2N,HCl,H_2O$, needles, m. p. 222°). From its *methiodide*, $C_{20}H_{28}O_2NI$, needles, m. p. 238°, by treatment with potassium hydroxide, trimethylamine and 3-*methoxy*-5-*vinylhexa*-

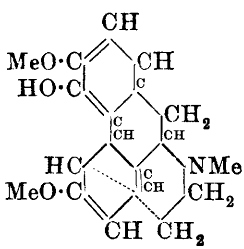
hydrophenanthrylene oxide (annexed formula), $C_{17}H_{18}O_2$, prisms, m. p. 80°, were obtained. The latter compound gives an oily dibromide, and, by reduction in presence of palladium, 3-*methoxy*-5-*ethylhexahydrophenanthrylene oxide*, prisms, m. p. 69°. *Dehydroxytetrahydrocodeine*, $C_{18}H_{25}ON_2,\frac{1}{2}H_2O$, needles, m. p. 144—145°, $[\alpha]_D^{18}$ −36·92°, is the second product of reduction of β-chlorocodide, and is also obtained by Clemmensen's method from *dihydrocodeinone*, $C_{18}H_{21}O_3N$, prisms, m. p. 193—194° (*hydrochloride*, $C_{18}H_{21}O_3N,HCl,2H_2O$, m. p. 82°; *oxime*, $C_{18}H_{22}O_3N_2$, m. p. 266°), which is itself obtained from codeinone by reduction in presence of palladium. Dehydroxytetrahydrocodeine gives a *methiodide*, $C_{19}H_{28}O_2NI$, needles, m. p. 256°, but no acetyl or benzoyl derivative. J. K.



The Reduction Products of Thebaine. MARTIN FREUND and EDMUND SPEYER [with ERNST GUTTMANN] (*Ber.*, 1920, **53**, [*B*], 2250—2264).—By reduction of thebaine with sodium and alcohol, Freund has already obtained a phenolic dihydrothebaine with m. p. 154° (A., 1899, i, 309). Reduction in cold *N*-hydrochloric acid by means of spongy platinum gives a new dihydrothebaine with m. p. 162—163°, which is insoluble in sodium hydroxide. If thebaine is expressed by the formula (I), then the older and newer reduction products are most probably denoted by the formulæ (II) and (III) respectively. The reactions of the new product are described.



(I.)



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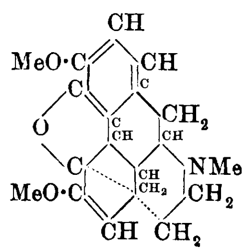
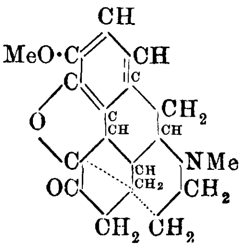


(III.)

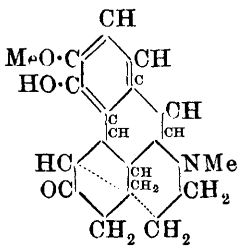
Dihydrothebaine (III) crystallises in prismatic tablets, m. p. 162—163°, and forms a *hydrochloride* (the base is boiled with ammonium chloride), a *picrate*, m. p. 235°, and a *methiodide*, $C_{19}H_{23}O_3N,MeI,2H_2O$, needles, m. p. 231°. The last salt yields a *de*-N-*methyldihydrothebaine*, $C_{20}H_{25}O_3N$, tablets, m. p. 134—135°, when boiled with 5% sodium hydroxide, and this base gives a *methiodide*, feathery groups of needles, m. p. 243°, which is, in turn, decomposed into trimethylamine and a phenanthrene *compound*, $C_{17}H_{16}O_3$, colourless cubes, m. p. 150—151°, by boiling with amyl-alcoholic potassium hydroxide.

Cyanogen bromide converts the base into *cyanodihydronorthebaine*, [N·CN instead of NMe], which crystallises in stout columns, m. p. 258—259°. Hydrogen peroxide (30%) produces an oily amine-oxide [NMe:O], which is characterised by a *picrate*, nodules of needles, m. p. 209—210°.

When hydrolysed by hydrochloric acid, the base yields methyl alcohol and *dihydrocodeinone* (annexed formula). This crystallises in columns, m. p. 197—198°, and yields a *hydrochloride*, a *hydriodide*, long needles, m. p. 219—220°, a *methiodide*, leaflets, m. p. 255°, an *oxime*, decomp. 264°, and a *phenylhydrazone*, $C_{24}H_{27}O_2N_3$,EtOH, elongated columns, m. p. 106—107°. The methiodide is transformed by boiling with dilute sodium hydroxide into *de*-N-*methyldihydrocodeinone*, stout prisms, m. p. 120—121°, and this gives a *methiodide*, $C_{19}H_{23}O_3N$,MeI, m. p. 280°, which loses trimethylamine when boiled with concentrated alkali hydroxide. Dihydrocodeinone also reacts with cyanogen bromide to form *cyanodihydronorcodeinone*, m. p. 224—225°, and with 30% hydrogen peroxide to give an amine-oxide, which yields a *picrate*, m. p. 231—232° (decomp.).



If thebaine is hydrogenated by means of colloidal palladium, reduction proceeds further. The same product is obtained by reducing dihydrothebaine with sodium and amyl alcohol, or by means of colloidal palladium, and it is found to be *dihydrothebainone* (annexed formula). It crystallises in leaflets, m. p. 150—151°, forms a *hydrochloride*, $[\alpha]_D$ −50·71°, a *hydriodide*, leaflets, decomp. 262—263°, a *methiodide*, m. p. 150°, and an *oxime*, m. p. 253—255° (*hydrochloride*, m. p. 318°). The methiodide is converted as above into *de*-N-*methyldihydrothebainone*, stout columns, m. p. 183°, $[\alpha]_D$ +60·7°, which forms a *hydriodide*, m. p. 180°.



J. C. W.

Preparation of Dialkylaminoethyl Derivatives of Theobromine. Société Chimique des Usines du Rhône (Brit. Pat. 155748).—Dialkylaminoethyl derivatives of theobromine are obtained by the action of chloroethyldialkylamines on metallic salts of theobromine. Thus *diethylaminoethyltheobromine*, m. p. 67°, is obtained by boiling for several hours sodium theobromine (20 parts) suspended in benzene with chloroethyldiethylamine (15 parts). The base gives a neutral water-soluble hydrochloride by evaporating to dryness a solution in the theoretical quantity of hydrochloric acid. It crystallises from alcohol in fine, colourless crystals, m. p. 202°. This salt has the advantages over other

soluble derivatives of theobromine that, whilst possessing all the therapeutic properties of this substance, it has no irritating effect on the tissues. G. F. M.

Synthesis of Pyrrole Compounds from Dihydropyridine Derivatives. ERICH BENARY (*Ber.*, 1920, **53**, [*B*], 2218—2224).—When ethyl 2 : 6-dimethyl-4-chloromethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate (A., 1911, i, 320; 1918, i, 350) is boiled with potassium cyanide and alcohol it is transformed into a mixture of *ethyl* 2 : 6-*dimethyl*-4-*cyanomethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* (I), glistening leaflets, m. p. 106—107°, sparingly soluble in alcohol, and freely soluble *ethyl* 5-*methyl*-3-*cyanomethylpyrrole*-2-*carboxylate* (II), soft needles, m. p. 150°. The latter compound is derived from the former, and can be prepared from it in more than 70% yield by boiling with alcoholic potassium hydroxide. The mechanism of the reaction is difficult to define, but is probably represented thus:

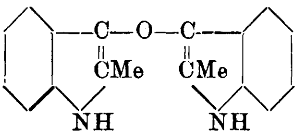
$$NH{<}\begin{matrix}CMe{:}C(CO_2Et)\\ CMe{:}C(CO_2Et)\end{matrix}{>}CH\cdot CH_2\cdot CN \xrightarrow[-2EtOH,\ -CO_2]{+2H_2O}$$
(I.)

$$NH{<}\begin{matrix}C(CO_2Et){:}C\cdot CH_2\cdot CN\\ CMe{=\!=\!=}CH\end{matrix}$$
(II.)

The ester (II) is hydrolysed by prolonged boiling with alcoholic potassium hydroxide, and the 5-*methyl*-3-*cyanomethylpyrrole*-2-*carboxylic acid* forms microscopic needles, decomp. 264°. Neither the ester nor the acid respond to the pine-shaving test, but if the acid is distilled with sand, it changes into 5-*methyl*-3-*pyrrylacetonitrile* (5-*methyl*-3-*cyanomethylpyrrole*), colourless needles, m. p. 87—89°, which does give the test and yields 3 : 5-dimethylpyrrole when distilled with powdered potassium hydroxide. The acid also forms a *mixed anhydride*, $NH{<}\begin{matrix}C(CO\cdot OAc){:}C\cdot CH_2\cdot CN\\ CMe{=\!=\!=}CH\end{matrix}$, when boiled with acetic anhydride; this melts at 149—150°, evolves acetic acid, and changes into the normal *anhydride*, $C_{16}H_{14}O_3N_4$, decomp. 290°. The α-carbon atom in the above 5-methyl-3-cyanomethylpyrrole is very reactive, for the nitrile condenses readily with formaldehyde to give 5 : 5′-*dimethyl*-3 : 3′-*dicyanomethyl*-2 : 2′-*dipyrrylmethane*, colourless needles, m. p. 330°. J. C. W.

Indole Group. VII. Products of the Auto-oxidation of Indoles. BERNARDO ODDO (*Gazzetta*, 1920, **50**, ii, 268—275. Compare A., 1916, i, 502).—The auto-oxidation of 2-methylindole is best effected by spreading out the powdered compound in the air and moistening it from time to time with an organic solvent such as alcohol or ether. The product of the oxidation crystallises in microscopic, yellow prisms, m. p. 208—209°, its composition and its molecular weight in boiling acetone or methyl alcohol being in agreement with the formula $C_{18}H_{16}ON_2$. The melting point and the

behaviour towards solvents correspond with those of the compound which Plancher and Colacicchi obtained (A., 1911, i, 566) by oxidising 2-methylindole with the help of hydrogen peroxide or monopersulphuric acid, and to which they attributed the structure (I). Of the other possible constitutions for this compound, (II)

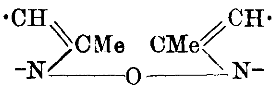


(I.)

$$\begin{matrix}-CH\\-NH\end{matrix}\!\!>C\cdot CH_2\cdot O\cdot CH_2\cdot C\!<\!\!\begin{matrix}CH-\\NH-\end{matrix}$$

(II.)

is excluded by the observation that the action of reducing agents results in the ready formation of dihydromethylketole (Jackson, A., 1881, 734; Bamberger and Sternitzki, A., 1893, i, 520). On the other hand, the yellow colour of the compound and its colour reactions with sulphuric acid and with acetic acid indicate that it is a derivative of indoxyl rather than of 1-oxindole (annexed formula) (*loc. cit.*). The behaviour of the compound towards a solution of magnesium ethyl iodide shows that the molecule contains active hydrogen (A., 1907, i, 549; A., 1911, ii, 826), 1·76 atoms being found in place of 2 atoms calculated for $C_{18}H_{14}O(:NH)_2$. When boiled for an hour with concentrated alkali hydroxide solution, the compound undergoes no change. The formula I is regarded as the correct one.



Auto-oxidation of scatole in alcoholic solution yields in small proportion a dark, pulverulent compound, m. p. about 245° (decomp.), which dissolves readily in concentrated sulphuric acid and sparingly in concentrated hydrochloric acid, giving pale chestnut solutions.

The action of oxygen on the magnesium derivative corresponding with 2-methylindole appears to give rise to a peroxide, $NH<\!\!\begin{matrix}C_6H_4\\CMe\end{matrix}\!\!>C\cdot O\cdot OMgX$, rather than to a compound of the alkyloxide type (compare Angeli and Pieroni, A., 1919, i, 134). Treatment of the oxidation product of magnesium ethyl bromide with benzoyl chloride gives rise to ethyl perbenzoate: $EtO\cdot O\cdot MgBr + Ph\cdot COCl = EtO\cdot OBz + MgBrCl$. This peroxide mostly decomposes during distillation, with slight explosions, into ethyl benzoate and oxygen, but both the undistilled product of the reaction and also the portion distilling below 100° respond to the reactions for peroxides. T. H. P.

4-Nitrophenazoxine. F. Kehrmann and Marie Ramm (*Ber.*, 1920, **53**, [*B*], 2265—2267).—Ullmann and Kuhn prepared 5-nitrophenazoxine by condensing 1-chloro-2:6-dinitrobenzene with *o*-aminophenol and heating the diphenylamine derivative with sodium hydroxide (A., 1909, i, 473). Starting with 1-chloro-2:4-dinitrobenzene, the authors have obtained the *sodium* salt of 2:4-di-

nitro-2′-hydroxydiphenylamine as pale brown leaflets, but have experienced much difficulty in effecting the desired ring closure, a small yield being obtained by heating the salt with sodium acetate in glycerol. 4-*Nitrophenazoxine* crystallises in dark brown needles with brassy lustre, decomp. 200—300°, gives yellow solutions with striking yellowish-green fluorescence in benzene and ether, reddish-brown solutions in sulphuric acid and violet in alcoholic alkali, and forms an *acetyl* derivative, m. p. 135·5°. Reduction by means of stannous chloride furnishes the double salt of 4-aminophenazoxine, which may be oxidised to the known 4-aminophenazoxonium salts.

J. C. W.

The Catalytic Hydrogenation of Hydrobenzamide. Method of Preparation of Benzylamine. GEORGES MIGNONAC (*Compt. rend.*, 1920, **171**, 1148—1150).—In the catalytic hydrogenation of hydrobenzamide by shaking it either in the pure state or in alcoholic solution in the presence of finely divided nickel in an atmosphere of hydrogen, the author considers that the first action is the scission of the molecule with the consequent formation of benzylideneimine,

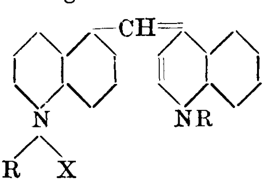
$$CHPh(N{:}CHPh)_2 + H_2 = CHPh{:}N{\cdot}CH_2Ph + CHPh{:}NH.$$

The imine then partly condenses with the elimination of ammonia and the formation of hydrobenzamide, whilst the remainder is hydrogenated to give benzylamine. In alcoholic solution the imine is for the most part hydrolysed and the yield of benzylamine is very poor.

For the preparation of benzylamine the hydrobenzamide should be hydrogenated at 15—18° without the use of a solvent. The benzylbenzylideneamine in the product is hydrolysed by acids to give benzylamine and benzaldehyde, the latter being used to prepare more hydrobenzamide.

W. G.

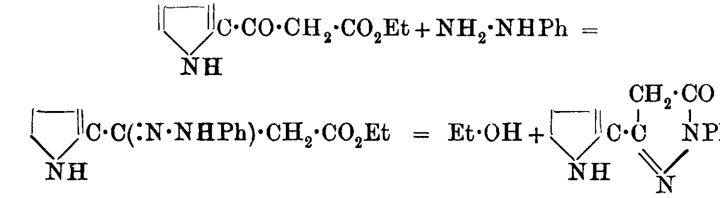
Kryptocyanines. A New Series of Photo-sensitising Dyes. ELLIOT Q. ADAMS and HERBERT L. HALLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2661—2663).—When lepidine ethiodide is dissolved in boiling alcohol and a solution of sodium ethoxide and formalin is slowly added after expelling the air by alcohol vapour, a photo-sensitising dye of a class designated "*kryptocyanines*," and referred to as "K III," is formed. It separates on cooling as a purple-black powder, has an absorption-maximum near 7000 Å. units, and a sensitisation-maximum near 7400 Å. Similar dyes, but not so good, are produced by substituted lepidines, and the class may perhaps be represented by the annexed formula.



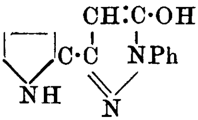
J. C. W.

New Syntheses in the Pyrrole Group. XIII. Pyrrolic Ketonic Acids and Dipyrryl Ketone. BERNARDO ODDO (*Gazzetta*, 1920, **50**, ii, 258—268).—With phenylhydrazine in alco-

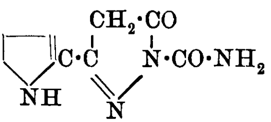
holic solution, ethyl pyrroylacetate (Oddo and Moschini, A., 1912, i, 804; Oddo and Dainotti, A., 1912, i, 721) reacts, readily yielding 1-phenyl-3-pyrrylpyrazolone, thus:



When treated with a crystal of sodium nitrite and a few drops of dilute hydrochloric acid, an alcoholic solution of this pyrazolone assumes a garnet-red coloration, changing to yellow on addition of alkali. With ferric chloride the alcoholic solution gives a red coloration with a yellow tinge, so that the phenylpyrrylpyrazolone is able to assume the tautomeric enolic form (annexed formula).



With semicarbazide the alcoholic solution of ethyl pyrroylacetate reacts less easily, the products consisting of the semicarbazone and of a small proportion of another compound, which is possibly 3-pyrrylpyrazolone-1-carbamide (annexed formula).



When heated in a sealed tube with absolute alcoholic ammonia, ethyl pyrroylacetate is converted into the corresponding amide, pyrroylacetamide.

Pyrrylglyoxylic acid (compare Ciamician and Dennstedt, A., 1885, 378; Oddo, A., 1910, i, 426; 1912, i, 803) may be obtained as ethyl ether in 91% yield by the action of ethyloxalyl chloride on magnesium pyrryl bromide:

$$MgBr\cdot C_4H_4N + COCl\cdot CO_2Et = MgBr\cdot CCl(CO_2Et)\cdot C_4H_4N \longrightarrow CO_2Et\cdot CO\cdot C_4H_4N + MgClBr.$$

Dipyrryl ketone was obtained by Ciamician and Magnaghi (A., 1885, 809) as a secondary product of the interaction of carbonyl chloride and the potassium derivative of pyrrole, the chief product being carbonylpyrrole or tetrolcarbamide, $C_4H_4N\cdot CO\cdot C_4H_4N$. The author finds that dipyrryl ketone forms the sole product of the action of pyrroyl chloride (Oddo and Moschini, A., 1912, i, 803) on a magnesium pyrryl compound in ethereal solution.

1-*Phenyl*-3-*pyrrylpyrazolone*, $C_{13}H_{11}ON_3$, forms pink needles, m. p. 193°, dissolves in cold concentrated sulphuric acid to a garnet-red solution, and reacts vigorously with concentrated nitric acid, giving a blood-red solution, which deposits a dark red, gelatinous precipitate when diluted with water.

Ethyl pyrroylacetate semicarbazone,

$$C_4H_4N\cdot C(CH_2\cdot CO_2Et){:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in yellow needles, m. p. 90°, and gives no appreciable

coloration in alcoholic solution with either sodium nitrite and dilute hydrochloric acid or ferric chloride.

3-Pyrrylpyrazolone (?) forms yellow needles, m. p. 192°.

Pyrroylacetamide, $C_4H_4N\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, forms a white, nacreous, microcrystalline powder, m. p. 184°.

Ethyl pyrrylglyoxylate forms tabular crystals, m. p. 44·5°, apparently of the rhombic system, and has the normal molecular weight in freezing benzene. Pyrrylglyoxylic acid crystallises in aggregates of slender, yellow needles or plates, m. p. 113° (decomp.), probably of the monoclinic system; the silver salt forms colourless needles.

T. H. P.

Methylation by means of Diazomethane in the Uric Acid Series. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1920, **53**, [*B*], 2327—2342).—Contrary to expectation, diazomethane reacts quite readily with uric acid derivatives, and the results obtained have considerable theoretical interest. Uric acid itself, and 1-, 3-, 7-, 1:3-, 1:7-, 3:7-, and 1:3:7-methylated uric acids all give 2:6-dioxy-8-methoxy-1:3:7-trimethylpurine (8-methoxycaffeine), which changes into tetramethyluric acid when heated at 200°. Similarly, 1:3-dimethyl-7-ethyluric acid gives 2:6-*dioxy*-8-*methoxy*-1:3-*dimethyl*-7-*ethylpurine*, m. p. 135°, which changes at 200° into 1:3:9-*trimethyl*-7-*ethyluric acid*, m. p. 215°. On the other hand, 1:7:9-, 7:9-, 1:9-, and 9-methylated uric acids react in descending order of readiness (the last being especially sluggish) to give 6:8-*dioxy*-2-*methoxy*-1:7:9-*trimethylpurine*, m. p. 186—197°, which changes readily at 205° into tetramethyluric acid. Similarly, 1:7:9-trimethyluric acid reacts with diazoethane to give 6:8-*dioxy*-2-*ethoxy*-1:7:9-*trimethylpurine*, m. p. 149°, which changes at 230° into 1:7:9-*trimethyl*-3-*ethyluric acid*, m. p. 240—241°.

Uric acids with methyl in positions 3:9, 3:7:9, and 1:3:9 do not react at all.

The chief conclusions which may be drawn from the above summary are as follows: (1) The production of methoxy-derivatives illustrates the wandering of hydrogen from positions 3 and 9, especially from the latter. (2) The most active hydrogen is that in position 9, since if that in position 3 is still present, methyl enters at 8. Next in activity is the hydrogen in position 3, whilst if the atoms in positions 3 and 9 are already replaced, those in 1 and 7 are quite indifferent.

With the above, also, the third and fourth of the four possible trimethylethyluric acids have become known.

The uric acid glycols, their mono-ethers, and their di-ethers behave in three distinct ways towards diazomethane. In the case of the mono-alkyl ethers, methyl enters position 9 unless the hydrogen has already been replaced, when no reaction takes place. The products are *N*-methyl, and not methoxy-derivatives. The di-ethers take up methyl in position 1 unless this has no free hydrogen, whilst the free glycols give mono-methyl ethers, which may be isolated if there is no free hydrogen in position 9.

4-Hydroxy-5-methoxy-1:3-dimethyl-4:5-dihydrouric acid yields

4-*hydroxy*-5-*methoxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, long, quadratic prisms, m. p. 194°; the ethyl ether gives 4-*hydroxy*-5-*ethoxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, small, elongated, rectangular leaflets, m. p. 138°; the 3 : 7-methyl derivative gives 4-hydroxy-5-methoxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid (A., 1917, i, 299); the appropriate 7-alkyl derivatives yield 4-*hydroxy*-5-*ethoxy*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, m. p. 185°, and 4-*hydroxy*-5-*ethoxy*-9-*methyl*-7-*ethyl*-4 : 5-*dihydrouric acid*, m. p. 193°. 4 : 5-Dimethoxy-4 : 5-dihydrouric acid gives 4 : 5-dimethoxy-1-methyl-4 : 5-dihydrouric acid (A., 1916, i, 293); the 3 : 7-dimethyl derivative yields the well-known 4 : 5-dimethoxy-1 : 3 : 7-trimethyl-4 : 5-dihydrouric acid; the 7 : 9-compound gives 4 : 5-*dimethoxy*-1 : 7 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, m. p. 152°; the 3 : 9-compound yields 4 : 5-*dimethoxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, large, rhombic tablets, m. p. 128°. 4 : 5-Dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid gives 4-*hydroxy*-5-*methoxy*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, m. p. 185°, and the 3 : 7-compound yields the above 4-hydroxy-5-methoxy-3 : 7 : 9-trimethyl-4 : 5-dihydrouric acid. [Most of these new compounds have been prepared by other means, which will be described soon in the *Annalen*.]

1 : 7-Dimethyl*spiro*hydantoin, from 3 : 9-dimethyluric acid, reacts readily with diazomethane to give tetramethyl*spiro*hydantoin (A., 1911, i, 240). J. C. W.

Intramolecular Condensations by means of the Oxyazo-group. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 365—368).—When heated in concentrated sulphuric acid solution under the conditions which determine conversion of azoxy- into hydroxyazo-compounds, *o*-aminoazoxybenzene loses a molecule of water, giving the internal anhydride, phenylaziminobenzene, $NH_2\cdot C_6H_4\cdot N\colon NPh\colon O \longrightarrow C_6H_4{<}{\overset{N}{\underset{N}{|}}}{>}NPh + H_2O$.

This reaction is analogous to the formation of a homologue of phenylaziminobenzene by the cautious oxidation of *o*-aminoazotoluene by chromic acid (Zincke, A., 1886, 236), except that the oxygen is supplied by the oxyazo-group, $\cdot N\colon NO\cdot$. More than 90% of the *o*-aminoazoxybenzene employed undergoes the above reaction; a small proportion of it is subjected to Wallach's transposition, yielding 2-amino-4′-hydroxyazobenzene,

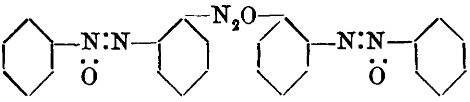
$$NH_2\cdot C_6H_4\cdot N\colon N\cdot C_6H_4\cdot OH,$$

previously unknown. The yield of azo-compound may be increased somewhat by protecting the amino-group of the *o*-aminoazoxybenzene by introduction of an acetyl residue, but even then the formation of phenylaziminobenzene predominates.

With *o*-hydroxylaminoazoxybenzene, also, a molecule of water may be eliminated from the two nitrogenated residues, with formation of the oxide of phenylaziminobenzene, that is, aznitrosobenzene,

$$OH\cdot NH\cdot C_6H_4\cdot N\colon NPh\colon O \longrightarrow C_6H_4{<}{\overset{N-}{\underset{NO}{|}}}{>}NPh + H_2O.$$

This reaction is realised by treating the hydroxyamino-compound in alcoholic solution with a trace of sodium hydroxide (compare Werner and Stiasny, A., 1900, i, 194); under these conditions, however, a considerable proportion of the hydroxylaminoazobenzene undergoes a transformation which occurs with aromatic β-hydroxylamines, yielding a trisazoxybenzene, which, on the basis of the structure assigned to the parent compound (A., 1920, i, 886), has the annexed formula.



In these two new intramolecular condensations, the oxyazo-group, $\cdot N\colon NO\cdot$, acts on the amino- or the hydroxylamino-residue in the same way as the nitro-group acts on the hydrazo-group, $\cdot NH\cdot NH\cdot$.

2-*Amino-4′-hydroxyazobenzene*, $C_{12}H_{11}ON_2$, crystals, m. p. 159°, forms a slightly soluble, yellow sodium salt and a readily soluble, blood-red potassium salt, and gives red and green salts with concentrated and moderately concentrated acids respectively. When treated in ethereal solution with hydrogen in presence of platinum-black, it yields *o*-phenylenediamine.

Trisazoxybenzene (see above), $C_{24}H_{18}O_3N_6$, forms transparent, sulphur-yellow, rhombic plates. T. H. P.

Preparation of some Hydrazines. LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1921, **37**, 7—11).—Sodium hyposulphite can be used with advantage in the preparation of hydrazine derivatives in place of hydrogen sulphites and stannous salts. Phenylhydrazine, for example, is obtained in more than 90% yield by treating a solution of phenyldiazonium chloride (1 mol.) with a concentrated solution of sodium hyposulphite (1 mol.) at 0° in presence of an excess of hydrochloric acid. Complete reduction immediately occurs, and the hydrazinesulphonate is hydrolysed to phenylhydrazine hydrochloride by boiling the solution for a few minutes with a further quantity of concentrated hydrochloric acid. The reactions are expressed by the equations $PhN_2Cl + Na_2S_2O_4 + H_2O = NHPh\cdot NH\cdot SO_3Na + NaCl + SO_2$ and $NHPh\cdot NH\cdot SO_3Na + HCl + H_2O = NHPh\cdot NH_2,HCl + NaHSO_4$. Phenylhydrazine-*p*-sulphonic acid is similarly obtained with a yield of about 60% of the theoretical by reduction of diazotised sulphanilic acid with the theoretical quantity of hyposulphite solution. The reduction of *p*-nitrophenyldiazonium chloride by means of hyposulphite is best carried out in alkaline solution. The product is a mixture of the sodium salt of *p*-nitrophenylhydrazine and a small quantity of the hydrazinedisulphonate. After hydrolysing the latter by boiling with concentrated hydrochloric acid, the base is isolated in the usual way, the yield amounting to 95% of the theoretical. The substitution of titanous salts for stannous salts in the preparation of hydrazines is usually not successful, owing to the formation of a condensation product of the hydrazine and unchanged diazonium compound, which is not further reducible. The case of diazotised

m-nitroaniline is an exception, but the preparation of *m*-nitrophenylhydrazine by this method has no advantages over other methods. Similar condensation products are formed when stannous salts or sulphites are used as reducing agents in half the proportion theoretically required for the complete reduction to the hydrazines. G. F. M.

Nitrosophenylhydroxylamine, Nitrosoacetanilides, and "Diazoanhydrides." EUG. BAMBERGER [with (Frl.) PAULA KÖPCKE] (*Ber.* 1920, **53**, [*B*], 2308—2320).—A discussion on these compounds is supported by experimental evidence obtained by Köpcke (*Diss.*, Zurich, 1899).

The action of mineral acids on nitrosophenylhydroxylamine was expressed originally in the equation NO·NPh·OH=NOPh+NOH (A., 1894, i, 412). The hypothetical NOH, or its decomposition products, has a powerful diazotising action, even on nitrosobenzene (A., 1918, i, 353), and this agrees with Köpcke's experiments. By submitting an ethereal solution of nitrosophenylhydroxylamine to the action of dry hydrogen chloride in the cold, she obtained evidence of the formation of nitrosobenzene, phenyldiazonium and *op*-dichlorophenyldiazonium salts (precipitated by β-naphthol), and only a trace of an arylhydroxylamine. Similarly, *p*-bromonitrosophenylhydroxylamine gave *p*-bromonitrosobenzene, probably *pp'*-dibromoazoxybenzene, and evidence of *p*-bromo- and *o*-chloro-*p*-bromo-benzenediazonium salts.

The reactions of nitrosoacetanilides and related compounds can generally be explained by assuming the formation of additive compounds (A., 1897, i, 241). Thus, nitrosodiphenylcarbamide and benzene give diphenyl,

$$\mathrm{NHPh{\cdot}CO{\cdot}NPh{\cdot}NO} + C_6H_6 \longrightarrow \mathrm{NHPh{\cdot}CO{\cdot}NPh{\cdot}NPh{\cdot}OH} \longrightarrow C_{12}H_{10},$$

and β-naphthol yields benzeneazo-β-naphthol. p-*Bromo*-N-*nitrosoacetanilide*, long, pale yellow needles, m. p. 87° (decomp.), reacts with benzene to form *p*-bromodiphenyl, with β-naphthol to give *p*-bromobenzeneazo-β-naphthol, and with α-naphthylamine to yield *p*-bromobenzeneazo-α-naphthylamine. *p*-Chloronitrosoacetanilide also gives *p*-chlorodiphenyl and *p*-chlorobenzeneazo-β-naphthol.

The action of alkali hydroxides on nitrosoacetanilides usually leads to the formation of *syn.*-diazohydroxides, but an experiment is mentioned in which *p*-chloronitrosoacetanilide was successfully converted into the explosive *p*-chlorobenzenediazoanhydride. These anhydrides are most probably, therefore, the precursors of the diazohydroxides. Indeed, if sodium hydroxide is added to a cold solution of diazotised anisidine, a yellow, explosive precipitate is obtained before sufficient alkali has been added to combine with the diazonium hydroxide. This raises the question of the constitution of the "diazoanhydrides," and the author gives arguments in favour of the diazobenzene formula, $C_6H_4{:}N_2$. Thus the action

of alkali on *p*-chloronitrosoacetanilide is represented by the scheme $C_6H_4Cl\cdot NAc\cdot NO \longrightarrow AcOH + C_6H_3Cl{:}N_2 \rightleftharpoons C_6H_4Cl\cdot N_2\cdot OH$.
J. C. W.

Arylnitroamines. EUG. BAMBERGER (*Ber.*, 1920, **53**, [*B*], 2321—2327).—The potassium salt of benzenediazohydroxide is conveniently made by mixing ethyl nitrate with a solution of potassium in alcohol and ether, and seventy to eighty seconds later adding aniline. The salt may be transformed into the barium salt and then into the free acid, phenylnitroamine (A., 1893, i, 327; 1894, i, 238). The acid is not quite pure, however, the impurity probably being a most explosive acid or ψ-acid, which is formed when the aniline is added at the same time as the ethyl nitrate. Reduction of phenylnitroamine to *iso*diazobenzene is best effected by means of zinc dust and very dilute ammonium chloride.

The methyl esters of the diazohydroxides evolve formaldehyde when carefully heated. This is also characteristic of benzeneazonitronic esters and certain amine-oxides, and reveals a similarity in constitution between the three classes, thus: $ArN{:}NO\cdot OMe$, $PhN{:}N\cdot CR{:}NO\cdot OMe$, and $R\cdot NMe_2O$.

[With ANTON VON GOLDBERGER (*Diss.*, *Zurich*, 1897).]—5-Nitro-*m*-4-xylidine is diazotised, and the solution treated with concentrated potassium hydroxide, so as to produce *potassium* 5-*nitro*-m-4-*xylene*iso*diazo-oxide*, $NO_2\cdot C_6H_2Me_2\cdot N_2\cdot OK$, which crystallises in pale yellow leaflets. This is oxidised by potassium ferricyanide with some difficulty, the products being 5-*nitro*-m-4-*xylylnitroamine*, $NO_2\cdot C_6H_2Me_2\cdot NH\cdot NO_2$, long, glassy, straw-yellow needles, m. p. 90—91°, and 5-nitro-*m*-xylene. The nitroamine is not transformed into a nuclear-nitrated aniline when dissolved in a mixture of sulphuric and acetic acids, but reduced to the corresponding diazonium salt, since the diluted solution couples with β-naphthol to give the nitroxyleneazo-dye.

m-*Nitrophenylnitroamine* is also described, as pale yellow, glistening needles, m. p. 92°.
J. C. W.

The Mechanism of the Formation of Methæmoglobin through Acetanilide and its Derivatives. PHILIPP ELLINGER (*Zeitsch. physiol. Chem.*, 1920, **111**, 86—125).—From various experiments with acetanilide and some of its derivatives in vivo and in vitro, it is considered highly probable that the formation of methæmoglobin from hæmoglobin by the action of acetanilide depends on the intermediate formation of acetylphenylhydroxylamine from the acetanilide by contact with animal tissue. This, like all hydroxylamines, acts as a strong methæmoglobin builder. Similarly, aceto-*o*-toluidide and phenacetin also act as methæmoglobin builders indirectly.
S. S. Z.

Nitrite Methæmoglobin and Related Pigments. H. HARTRIDGE (*J. Physiol.*, 1920, **54**, 253—259).—Nitrite methæmoglobin is a definite chemical compound; the evidence is mostly spectroscopic.
G. B.

The Urine Pigments. II. Urochromogen. M. WEISS (*Biochem. Zeitsch.*, 1920, **112**, 61—97, 324. Compare A., 1911, ii, 136).—Urochromogen is an acid, and readily forms salts with the alkalis and alkaline earths. Certain of its reactions suggest that it is a phenylalanine derivative containing a hydroxyl group in the ortho-position, but other more complex groups would seem also to be present. S. S. Z.

New Methods for the Preparation of Nucleic Acids. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1920, **111**, 257—272. Compare this vol., i, 76).—The nucleoprotein from the pancreas was prepared by digesting the minced organ with hot water and treating the aqueous extract with sodium hydroxide, filtering, and precipitating with 96% alcohol after neutralisation with acetic acid. The nucleoprotein was then hydrolysed with sodium hydroxide, and the mixed nucleic acids precipitated with 96% alcohol; these were purified by precipitation with alcohol in alkaline solution. The two nucleic acids were separated by salting out the sodium salt of guanylic acid with sodium acetate. The tertiary salt of guanylic acid was prepared by treating the secondary sodium salt of the acid with sodium hydroxide and precipitating with 96% alcohol. S. S. Z.

A New Method of Cleavage of Nucleic Acids. H. STEUDEL and E. PEISER (*Zeitsch. physiol. Chem.*, 1920, **111**, 297—303).—Sodium nucleate from the sperm of the herring was hydrolysed with a calcium hydrogen sulphite solution (prepared by passing sulphur dioxide through a suspension of 3% of calcium carbonate in water) at 120—130° for two hours. The resulting products of hydrolysis were precipitated with calcium acetate and purified by various precipitations. From the phosphorus and nitrogen determinations, it was found that the precipitated substance was identical with thymic acid. On hydrolysis with sulphuric acid under reflux, thymin was obtained from it. The above method offers the opportunity of preparing thymic acid with comparative ease, and the acid thus obtained shows great stability. After more than a year, it retained its white colour, solubility in water, and reducing power for Fehling's solution. S. S. Z.

The Free Amino-groups of the Proteins. II. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1919, **108**, 287—294).—The "formol value" and the "methyl value" obtained by methylating with methyl sulphate were determined in gelatin and casein digested with pepsin and in gliadin and zein digested with hydrochloric acid and in some undigested proteins. The relation of the figures obtained to the free amino-groups in the protein molecule is discussed. S. S. Z.

Ion Series and the Physical Properties of Proteins. II. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **3**, 247—269. Compare A., 1920, i, 894).—The results of this work show that the Hofmeister

series is not the correct expression of the relative effects of ions on the swelling of gelatin, and that it is not true that chlorides, bromides, and nitrates have "hydrating," and acetates, tartrates, citrates, and phosphates "dehydrating," effects. If the hydrogen-ion concentration of the gelatin is the same, the swelling is the same for all these ions, whilst it is considerably less for gelatin sulphate. These are the results that would be expected on the basis of the combining ratios of the corresponding acids with gelatin. Hence it is only the valency, and not the nature of the ion in combination with gelatin, which affects the degree of swelling. This is corroborated by experiments with alkalis.

J. C. D.

Deuterokeratose obtained from Horn by means of Digestion with Alkali. HEDWIG LANGECKER (*Zeitsch. physiol. Chem.*, 1919, **108**, 230—242).—Horn was digested with semi-normal and normal sodium hydroxide at 40°, neutralised with hydrochloric acid, filtered, and the filtrate saturated with sodium chloride in order to remove the protalbumoses. The deuterokeratose was precipitated from the filtrate of the sodium chloride saturated solution with acid. The rotation, as well as the amino-acid content by Van Slyke's method, was estimated in both hydrolysates. The deuterokeratose has been found to be resistant to the action of proteolytic enzymes. S. S. Z.

Serecin and the Estimation of its Constituents. WALTER TÜRK (*Zeitsch. physiol. Chem.*, 1920, **111**, 69—75).—Silk was treated with water at 145° for three hours under a pressure of three atmospheres, when serecin went into solution, and was precipitated from it with absolute alcohol. It was examined for the various colour reactions. The silk gelatin was then hydrolysed with sulphuric acid, and the amounts of the amino-acids obtained were: tyrosine 5·69%, leucine 1·79%, serine 6·81%, arginine 4·56%, lysine 1·69%, histidine 1·02%. S. S. Z.

Mechanism of Enzyme Action. I. Rôle of the Reaction of the Medium in Fixing the Optimum Temperature of a Ferment. ARTHUR COMPTON (*Proc. Roy. Soc.*, 1921, [B], **92,** 1—6).—The variation of the optimum temperature of an enzyme with the hydrogen-ion concentration of the medium, and its actual fixation for any given concentration of hydrogen ions, constitute but different expressions of the same phenomenon, being a consequence the one of the other. The optimum temperature of any ferment or ferment function occurring in a given enzyme preparation is independent of the concentration of the enzyme, the duration of the action, and the chemical reaction, or hydrogen-ion concentration of the medium, being constant. J. C. D.

The Significance of the Hydrogen Ion Concentration for the Digestion of Proteins by Pepsin. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1920, **3**, 211—227).—The rate of digestion and the conductivity of protein solutions are very closely parallel.

Evidence is presented in support of the hypothesis that the determining factor in the digestion of proteins by pepsin is the amount of ionised protein present in the solution.

It is clear that this hypothesis cannot be extended directly to enzymes in general, since in many cases the substrate is not known to exist in any ionised condition at all. J. C. D.

Action of Chymosin and Pepsin. VI. Preparation of Pure Stomach Enzymes and Observations on their Action. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1919, **108**, 243—286. Compare A., 1918, i, 456, 510).—On extracting the mucous membrane of the dog, pig, cow, or horse with 0·2% hydrochloric acid and mixing the clear, filtered infusion with an equal volume of a saturated solution of sodium chloride, a flocculent, hyalin substance is obtained. This substance contains the best part of the enzyme activity of the extract, and at dilutions of 1 : 10,000,000 was still active. It could be redissolved in dilute acid and reprecipitated with sodium chloride. After five precipitations, the fraction still showed strong activity. If the extraction is carried out at body temperature on the addition of the sodium chloride, a precipitate is formed after some time. It is considered that the substance is denaturated when extracted at 37—38°. The chymosin activity of the substance from various animals has been studied. S. S. Z.

Peroxydases. II. RICHARD WILLSTÄTTER (*Annalen*, 1921, **422**, 47—73. Compare Willstätter and Stoll, A., 1918, i, 555).—The enzyme contents of plant materials are compared by means of the "peroxydase number." This is the number of mg. of purpurogallin obtained when 5 grams of the plant material are worked up by the method previously described and the product made up to a 200 c.c. suspension, of which 5 c.c. are taken for estimation by the pyrogallol–hydrogen peroxide mixture; the peroxydase number × 40/5000 gives the purpurogallin number (*loc. cit.*).

The peroxydase number of horse-radish submitted to dialysis treatment (*loc. cit.*), initially 860, falls after four days to 601, and then increases after eighteen days to 1040. This variation of the peroxydase number is due, not to repression and stimulation of the enzymatic activity, but to formation of fresh peroxydase, so long as the plant cells retain their vitality; when the dialysis is effected with water containing toluene, the formation of new peroxydase does not occur, and the peroxydase number falls rapidly, owing to exosmosis of the enzyme. Similar phenomena have been observed in the case of other plant roots.

The peroxydase number of horse-radish attains its maximal value after dialysis for about three weeks, and from this it would appear that this duration of dialysis should result in the optimum yield of peroxydase extract. This, however, is not the case, all the evidence indicating that the plant material contains two peroxydases, the one easily soluble, the other quite insoluble, in water. Horse-radish is dialysed during several weeks, and, at definite

intervals, portions are removed and thoroughly extracted with water, the extract and the insoluble portion are separated in a centrifuge, and the peroxydase number of each determined. The amount of the soluble enzyme attains its maximal value after eleven days' dialysis; after four or five weeks it has fallen to less than two-thirds of its initial value, whilst the amount of the insoluble enzyme has increased to two and a-half times its initial value. For the preparation of the peroxydase, therefore, the plant material appears to be in the best state after dialysis for six to twelve days. The difference between the soluble and the insoluble peroxydase is probably one of chemical constitution. As these substances are regarded as glucosides, it is possible that a component of the peroxydase molecule is combined with a simple sugar to form the soluble peroxydase or with a more complex carbohydrate to form the insoluble peroxydase.

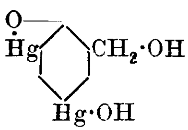
Based on the new experience gained, modifications of Willstätter and Stoll's method of extracting the crude peroxydase (*loc. cit.*) are described, the most important being the dialysis of the sliced roots for seven to nine days in water flowing at the rate of 100—150 litres per hour.

A further step has been made in the purification of the peroxydase preparation by means of adsorption experiments with aluminium or ferric hydroxide, silicic acid, kaolin, and talc. It has been found that a peroxydase preparation (purpurogallin number, 575) in solution in 50% alcohol at a concentration of 0·05% is almost completely adsorbed by aluminium hydroxide, and that 90—95% of the peroxydase is recovered in solution by agitating the adsorbate with water containing carbonic acid at 0—20°, the purpurogallin number of the recovered peroxydase being 1000—1100. The adsorption method gives the best results with peroxydase preparations having high purpurogallin numbers. A very great saving of time and trouble, however, can be effected and a preparation of great activity obtained as follows. The dialysis of the plant material, the digestion with oxalic acid and with barium hydroxide solution, and the removal of slimy substances by means of alcohol (*loc. cit.*) are effected as already described, but the aqueous-alcoholic filtrate (4—5 litres), instead of being evaporated to about 50 c.c., is freed from carbon dioxide by a current of air and treated with quantities of 20—30 c.c. of the adsorbent (3 grams of aluminium hydroxide suspended in 100 c.c. of water) every two or three minutes until 10—16 grams of aluminium hydroxide have been added. When the peroxydase reaction of a filtered portion is faint, a volume of alcohol equal to that of the aluminium hydroxide suspension introduced is added, the adsorbate is allowed to settle, the greater part of the solution is decanted, and the remainder centrifuged. The adsorbate is collected, treated with about 4 litres of twice-distilled water at 0°, and carbon dioxide passed in for about a quarter of an hour until the reaction is distinctly acid, the solution is filtered, the clear filtrate evaporated in a vacuum to 60—80 c.c., again filtered, and

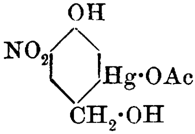
treated with five volumes of absolute alcohol, whereby 0·31 gram of peroxydase preparation (purpurogallin number, 860) is precipitated. C. S.

Oxidation of the Grignard Reagent. C. W. PORTER and CAROLYN STEEL (*J. Amer. Chem. Soc.*, 1920, **42**, 2650—2654).—An ethereal solution of magnesium phenyl bromide absorbs oxygen and gives rise to phenol, *p*-diphenylbenzene, *p*-benzoquinone, and *pp'*-dihydroxydiphenyl. The optimum temperature for the production of phenol is 0°, the yield being about 22·9%. Diphenyl is also formed, but its quantity does not vary if samples of the same solution are kept at different temperatures, from which it appears that it owes its origin to the Fittig reaction brought about by magnesium on the bromobenzene. The mechanism of some of the reactions is discussed and expressed as follows: (1) $PhMgBr + O_2 \longrightarrow PhO_2MgBr$; (2) $PhMgBr + PhO_2MgBr \longrightarrow 2PhOMgBr$; (3) $PhOMgBr + H_2O \longrightarrow PhOH + MgBr{\cdot}OH$; (4) $PhO_2MgBr + PhOMgBr \longrightarrow Ph_2O_2 + MgBr_2 + MgO$; (5) $Ph_2O_2 \longrightarrow OH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}OH$; (6) $Ph_2O_2 \longrightarrow Ph_2O + O$. The formation of phenyl ether was observed by Wuyts, who interpreted the reaction in a somewhat similar manner (A., 1909, i, 448). J. C. W.

Mercury Compounds of some Phenylcarbinols. MERRILL C. HART and ARTHUR D. HIRSCHFELDER (*J. Amer. Chem. Soc.*, 1920, **42**, 2678—2686).—When saligenin (15 grams) is boiled with a solution of mercuric acetate (80) for two hours and then left for several hours, it removes the whole of the mercuric ion, and forms an insoluble "*mercury saligenin*," probably of the annexed formula. This separates in masses of radiating needles, forms an insoluble chloride, slightly more soluble bromide and iodide, insoluble sulphate, and soluble nitrate, and dissolves in alkali hydroxides to form salts which separate as yellow solids on adding alcohol. It crystallises from hot acetic anhydride as a *triacetate*, $C_{13}H_{14}O_7Hg_2,H_2O$.



m-*Nitro*-p-*hydroxybenzyl alcohol*, $NO_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH$, long, yellow needles, m. p. 97°, also forms a *mercury* compound, which crystallises in long, pale yellow needles from 20% acetic acid, and yields an *acetate* of the annexed formula. The alcohol is obtained by the interaction of *o*-nitrophenol and bromomethyl alcohol (from formalin and hydrogen bromide) in the presence of zinc chloride. Non-phenolic aromatic alcohols, as far as was tested, and also *p*-nitrosaligenin, do not form mercury compounds.



These mercuriated compounds are about as powerfully antiseptic as mercuric chloride, but they are far less irritant. They are being used successfully in the treatment of gonorrhœa. J. C. W.

Physiological Chemistry.

Physical Exertion, Fitness, and Breathing. HENRY BRIGGS (*J. Physiol.*, 1920, **54**, 292—318).—Experiments carried out in a research on mine rescue apparatus. When exertion of steadily increasing magnitude (Martin's ergometer) is undertaken, the percentage of carbon dioxide in the expired air first rises and then, with an overload of work, falls. The crest of the curve is usually higher in the physically fit (up to 8·1% observed) than in the unfit (4·7%). The latter benefit from oxygen and exhale a greater percentage of carbon dioxide than when breathing air, even with normal loads. Extremely fit subjects receive no benefit from oxygen until the work becomes an overload. The divergence of the carbon dioxide curves when breathing (*a*) air, (*b*) oxygen, is a measure of the unfitness of the subject. The full benefit of oxygen is obtained with a 60% mixture, containing 40% nitrogen; purer oxygen gives no further advantage. The author compares the adaptation produced by physical training with that by life at high altitudes, and favours the theory that oxygen is actively secreted inwards by the lung epithelium (compare Douglas and Haldane, A., 1912, ii, 653). G. B.

Partition of Carbon Dioxide between Plasma and Corpuscles in Oxygenated and Reduced Blood. J. JOFFE and E. P. POULTON (*J. Physiol.*, 1920, **54**, 129—151).—The dissociation curves of oxygenated blood and of blood reduced to 10% oxygen saturation and the corresponding "true plasma" curves have been determined. At all pressures of carbon dioxide up to 600 mm. the "true plasma" contains more carbon dioxide than the corpuscles in equilibrium with it. With increase in the carbon dioxide pressure, acid migrates from the plasma into the corpuscles, and their dissociation curves are quite different from those of separated plasma and separated corpuscles, which constitutes a criticism of the method of van Slyke and Cullen (A., 1917, i, 521).

Reduced corpuscles and reduced true plasma contain respectively more carbon dioxide than oxygenated corpuscles and true plasma, the difference between the corpuscles being greater than the difference between the plasmas; so that if venous blood was completely reduced, the transport of carbon dioxide would be carried out chiefly by the corpuscles. Since venous blood is, however, usually not more than 40% reduced, the transport of carbon dioxide is actually carried out by corpuscles and plasma in nearly equal proportions. G. B.

Relation of Oxyhæmoglobin to the Carbon Dioxide of the Blood. J. M. H. CAMPBELL and E. P. POULTON (*J. Physiol.*, 1920, **54**, 152—166).—Within physiological limits of P_H all the carbon dioxide is present as bicarbonate; it does not combine with the blood proteins until the reaction is much more acid. The blood

proteins act as acids, competing with carbon dioxide for the sodium. Hæmoglobin has an acid dissociation constant of 2×10^{-8}. Its isoelectric point is $P_H = 6{\cdot}98$ (compare Straub and Meier, A., 1919, i, 53). At all pressures of carbon dioxide the corpuscles are more acid than the plasma; with increasing pressure the difference becomes less. The total sodium available for combining with carbon dioxide is $0{\cdot}03N$. G. B.

Carbon Dioxide Carrying Power of the Constituents of Plasma. The Alkali Reserve of Blood. J. MELLANBY and C. J. THOMAS (*J. Physiol.*, 1920, **54**, 178—191).—Lactic acid is produced from corpuscles in shed blood; hence (*a*) the steady fall in carbon dioxide of shed blood, (*b*) the possibility of abstracting carbon dioxide from blood and not from serum by a carbon dioxide vacuum, (*c*) the diminished capacity of blood, from which carbon dioxide has been removed, to re-combine with it. There is no evidence of ionic interchange between corpuscles and serum on freeing blood from carbon dioxide; the ash from normal blood and from blood freed from carbon dioxide combines with equal volumes of carbon dioxide. There is no evidence that the proteins of serum associate with sodium when carbon dioxide is removed from the blood. Coagulation of fibrinogen in blood or any fluid diminishes the capacity of the fluid to carry carbon dioxide, which is held by adsorption on the fibrinogen. Sodium hydrogen carbonate does not exist free in serum, since an equal volume of alcohol at $-10°$ precipitates it in association with the proteins, whilst it does not precipitate a protein-free solution of sodium hydrogen carbonate of the same strength (0·2%). The authors conclude that carbon dioxide in blood is combined (*a*) by adsorption on the proteins, and (*b*) as bicarbonate. The transport of carbon dioxide is effected by the protein. The alkali reserve is constituted by (*a*) bicarbonate, (*b*) protein. The "bicarbonate hypothesis" is inadmissible, since neither hæmoglobin nor the blood proteins function as weak acids sharing the available sodium with carbon dioxide (compare, however, Campbell and Poulton, preceding abstract). G. B.

Regulation of the Blood's Alkalinity. H. W. DAVIE, J. B. S. HALDANE, and E. L. KENNAWAY (*J. Physiol.*, 1920, **54**, 32—45).—The carbon dioxide dissociation curve is not quite in agreement with Parson's theory (A., 1919, i, 508) at high pressures. Ingestion of sodium hydrogen carbonate (up to 57·5 grams) produces alkalosis, which is compensated for by rapid excretion of the salt in the urine, disappearance of nearly all the urinary ammonia, and occasional appearance of acetone substances. The carbon dioxide capacity of the blood is increased, as is the alveolar carbon dioxide. G. B.

Colorimetric Determination of the Reaction of Blood by Dialysis. H. H. DALE and C. LOVATT EVANS (*J. Physiol.*, 1920, **54**, 167—177).—A collodion sac holding about 5 c.c. is filled with

oxalated blood and placed inside a glass tube of slightly larger diameter. The annular intervening space of about 1 c.c. contains physiological saline solution. Dialysis is complete in ten to fifteen minutes, when the P_H of the dialysate can be determined colorimetrically by mixing phosphate solutions until the mixture gives the same colour as the dialysate with neutral-red. For this purpose the dialyser and comparator tubes have flat bottoms made by cementing on a microscope slide. Escape of carbon dioxide during dialysis is prevented by a vulcanite collar to which the membrane is tied. This collar fits the dialysing tube, and is closed by a cork. The method is both convenient and accurate; the results agree closely with those obtained by means of a hydrogen electrode.

G. B.

Presence of Phosphates in Human Blood. XII. The Phosphorus Distribution according to the Known Methods of Separation and Isolation. JOH. FEIGL. (*Biochem. Zeitsch.*, 1920, **112**, 27—50).—A critical review of the literature on the subject. S. S. Z.

Observations on the Question of the Residual Reduction of the Blood. JOH. FEIGL (*Biochem. Zeitsch.*, 1920, **112**, 51—54). —A theoretical note in reference to the work of Ege (A., 1920, i, 781) and others. S. S. Z.

Oligodynamic Hæmolysis. W. HAUSMANN and W. KERL (*Biochem. Zeitsch.*, 1920, **111**, 122—123).—Silver, cadmium, copper, magnesium, nickel, lead, tin, and zinc produced hæmolysis when introduced into blood agar plates. S. S. Z.

The Kinetics of Inactivation of Complement by Light. S. C. BROOKS (*J. Gen. Physiol.*, 1920, **3**, 169—183).—The course of the inactivation of complement by light is that of a unimolecular reaction. It is thought that during this process a single disappearing molecular species governs the rate of reaction. J. C. D.

The Mechanism of Complement Action. S. C. BROOKS (*J. Gen. Physiol.*, 1920, **3**, 185—201).—Complement exposed to ultra-violet light is not sensitised thereby to the action of heat, which indicates that it is not a protein. The inactivation of complement by ultra-violet light is accompanied by a decrease in its surface tension, but is not apparently the result of any changes in hydrogen-ion concentration. Hydrogen-ion concentrations high enough to transform serum proteins past the isoelectric point permanently inactivate complement. On the basis of these and other observations it is suggested that there is present in serum a hæmolytic substance which is formed from a precursor and is constantly being formed and simultaneously broken down into inactive products. Both precursor and lysin contain the same photosensitive molecular group. The lytic substance is dependent for its activity on the state of the serum proteins. J. C. D.

Anti-substance Studies. III. The Chemical Nature of Anti-substances. F. M. HUNTOON, P. MASUCCI, and EDITH HANNUM (*J. Amer. Chem. Soc.*, 1920, **42**, 2654—2661).—The protective anti-substances in anti-pneumococcus serum were isolated by adding the antigen, allowing the anti-substances and antigen to unite, centrifuging, treating the sediment with reagents to separate the anti-substances again, and filtering through a candle filter. The clear, limpid solution of the anti-substances was tested in various ways, and from the results it may be gathered that anti-substances are (1) colloidal, since they do not dialyse, (2) not influenced by trypsin, (3) not globulins, (4) not soluble in ether, (5) not precipitated by 30% salt solution, (6) not injured by dilute acids or alkalis, (7) not affected by heat, below 60°. J. C. W.

Relationships between the Peptidolytic Activity of Intestinal Erepsin and the Chemical Constitution of the Substrate. A. CLEMENTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 327—329).—By means of the method of formaldehyde titration the author has investigated the action of intestinal erepsin from the dog or pig on cholylglycine, benzoylglycine, bromo*iso*hexoylglycine, and glycine anhydride. It is found that neither benzoylglycine, which normally is not present in the intestinal tube, nor cholylglycine, which normally passes with the bile from the liver into the intestine, is hydrolysed by the intestinal erepsin, and that bromo*iso*hexoylglycine, unlike leucylglycine, is also unattacked. In the case of glycine anhydride solutions, a slight increase in the aminic nitrogen is apparently caused by the intestinal erepsin, but this is regarded as due to the scission of glycylglycine previously formed rather than to the formation of a fresh quantity of glycylglycine; the conclusion is hence drawn that the erepsin is not capable of determining the rapid opening of the diketopiperazine ring of glycine anhydride.

These results, in conjunction with the behaviour of guanidylglycylglycine, show that suppression or absence or partial substitution of the free aminic group of the molecule of a polypeptide or similar compound may result in marked resistance of the CO·NH group to the hydrolysing action of erepsin. T. H. P.

Nitrogenous Equilibrium and Carbohydrates of the Food Ration. A. DESGREZ and H. BIERRY (*Compt. rend.*, 1920, **171**, 1393—1396).—From the results of feeding experiments with rats on diets of purified nutrients, free from vitamins, it is shown that if the carbohydrates are below a certain limit they cannot be replaced by any other type of nutrient. Nitrogen equilibrium can only be assured throughout a period of feeding if the diet contains a certain minimum of carbohydrate. W. G.

Nutrition of Protozoa. Effect of Substituting Uranium for Potassium in Growth Media. R. A. PETERS (*Proc. physiol. Soc.*, 1920, l—li; *J. Physiol.*, **54**).—*Colpidium* will

grow in ammonium glycerophosphate as the only source of nitrogen, carbon, and phosphorus. The statement that the animal organism requires a substance as complex as dextrose for its source of carbon is incorrect. Potassium is essential, and cannot be replaced by uranium (compare Zwaardemaker, A., 1917, i, 70, 105, 241; *Ann. Reports*, 1919, **16**, 148). G. B.

Radioactivity and Physiological Action of Potassium. ROBERT F. LOEB (*J. Gen. Physiol.*, 1920, **3**, 229—236).—The non-radioactive cæsium ion can replace the potassium ion almost quantitatively in solutions required for the development of the egg of the sea urchin into swimming blastulæ. Thorium chloride and uranium acetate cannot thus replace potassium chloride, nor do they antagonise the latter salt. J. C. D.

Chemical Character and Physiological Action of the Potassium Ion. JACQUES LOEB (*J. Gen. Physiol.*, 1920, **3**, 237—245).—It is shown that the ammonium ion acts in cases of antagonism on the egg of fundulus more like the potassium ion than the sodium ion, and this physiological effect is in harmony with the chemical behaviour of the three ions.

Evidence is given which indicates that the behaviour of the potassium ion in antagonistic salt action is due to its purely chemical character, that is, its atomic number, and not to those explosions in its nucleus which give rise to a trace of radioactivity. J. C. D.

The Relation of the Animal Cell to Electrolytes. J. GRAY (*J. Physiol.*, 1920, **54**, 68—78).—Living trout eggs, exposed to dilute hydrochloric acid ($N/200$—$N/500$), adsorb hydrogen, but not chlorine, ions. The former are replaced by a cation from the eggs (potassium?). The equilibrium is established by the outer membrane of the cell (Loeb's "membrane effect," A., 1918, i, 51). G. B.

A Lipotropic Mercury Compound. HANS HÜSGEN (*Biochem. Zeitsch.*, 1920, **112**, 1—22).—A method for the estimation of mercury in the brain is described. It consists of the destruction of the organic matter by heating with fuming sulphuric and fuming nitric acids, and electrolysing the mercury, which is afterwards volatilised into a capillary tube and weighed. The "lipotropic" mercury compound, "MAT" (4-*p*-tolueneazoacetanilide-3-mercuri-hydroxide, $C_6H_4Me\cdot N{=}N\cdot C_6H_3(NHAc)\cdot Hg\cdot OH$), when injected into rabbits, is taken up by the central nervous system, the muscles, and other organs much more readily than when ordinary mercury preparations are used. S. S. Z.

The Biochemical Behaviour of Glycollic and Oxalic Acids, especially against the Cells of Isolated Human Organs. ERNST SIEBURG and KARL VIETENSE (*Zeitsch. physiol. Chem.*, 1919, **108**, 207—229).—The action of the cells of various

human organs on glycollic acid and oxalic acid was studied. From glycollic acid, glyoxylic acid, formaldehyde, and succinic acid were formed by the cells of the different organs examined, but on no occasion was the formation of oxalic acid established. The oxalic acid was mostly recovered unchanged. S. S. Z.

Comparison of the Actions of *d*-, *l*-, and *i*-Camphor. IV. The Action on the Plain Muscle of the Leech. GEORG JOACHIMOGLU (*Arch. expt. Path. Pharm.*, 1920, **88**, 364—370. Compare A., 1917, i, 528).—Aqueous solutions of camphor in dilutions of 1:1000 to 1:5000 produce a marked increase in tonus and rhythmic contractions in the plain muscle of the leech. The action of the three isomeric camphors is identical. The pharmacological effect resembles that of santonin. Barium augments the action of camphor. The action of camphor on the leech is the same as that of thymol. S. S. Z.

Absorption and Elimination of Manganese Ingested as Oxides and Silicates. CLARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, **45**, 133—143).—Manganese oxide or silicate ores are soluble in gastric juice. Prolonged administration of manganese to dogs failed to produce any significant changes in manganese content of blood or tissues, or to cause any pathological symptoms. J .C. D.

The Behaviour of Substances of the Dibenzil Series (Dibenzyl, Hydroxybenzoin, Deoxybenzoin, Benzoin, Benzil, Benzilic Acid) in the Organism. ERNST SIEBURG and ERICH HARLOFF (*Zeitsch. physiol. Chem.*, 1919, **108**, 195—206). —When dibenzyl was fed to a rabbit, it was excreted in the urine as stilbene, m. p. 124°, in combination with glycuronic acid. Hydrobenzoin, deoxybenzoin, benzoin, and benzil were excreted as *o*-benzylbenzoic acid paired with glycuronic acid. Benzilic acid was obtained in the urine unaltered. No benzoic acid was found in the urine in any of the experiments. S. S. Z.

"Salbrantin": Intra-organic Behaviour of Halogenated Aromatic Compounds. EDUARDO FILIPPI (*Arch. Farm. sperim. Sci. aff.*, 1920, **30**, 113—126).—The results of the author's experiments are as follows. 3:5-Dibromosalicylic acid, m. p. 223°, is rapidly and completely destroyed either in vivo or in vitro, this ready decomposition being attributed to the presence in the molecule of a bromine atom in the para-position to the hydroxyl group. Similar behaviour is exhibited by 5-chloro-3-iodosalicylic acid, m. p. 224°, whereas 3:5-di-iodosalicylic acid gives up its halogen with some readiness, but is not completely destroyed.

"Salbrantin" gives up its bromine with the same rapidity and ease as 3:5-dibromosalicylic acid, and may therefore be regarded pharmacologically as a true brominated antipyrine, and not as a salicylic derivative. T. H. P.

The Oligodynamic Action of Metals. D. ACÉL (*Biochem. Zeitsch.*, 1920, **112**, 23—26).—Water which has been in contact with metallic silver for some time has been shown, by means of ammonium sulphide or of potassium chromate, to contain silver. It was also demonstrated that if this dissolved silver was removed, the water lost its oligodynamic action. The author therefore concludes that the oligodynamic action of silver is due entirely to the solubility of the metal in the water. S. S. Z.

The Magnesium-Calcium and the Barium-Sulphate Antagonism. M. KOCHMANN [with C. LUCANUS and R. MULTHAUPT] (*Biochem. Zeitsch.*, 1920, **112**, 291—309).—Sodium sulphate neutralises the toxic effect of barium chloride in the frog. Prophylactically, sodium chloride can neutralise several minimum lethal doses of barium chloride. Curatively, the sodium sulphate has to be administered between ten and thirty minutes after the injection of the barium chloride. It is supposed that the toxic barium ion is precipitated as barium sulphate. The above antagonistic action is discussed in comparison with the antagonistic action of magnesium and calcium. S. S. Z.

Variations in the Resistance of Protozoon Organisms to Toxic Agents. R. A. PETERS (*J. Physiol.*, 1920, **54**, 260—266). —Organisms from a culture of the ciliate protozoon *Colpidium*, when exposed to mercuric chloride (about $M/5000$), die in such a way that there is a straight-line relationship between the time and the logarithm of the percentage of survivors for a large part of the death process. The apparent logarithmic law (unimolecular reaction) can be interpreted in terms of the variation in the resistance of individuals, which are not entirely analogous to chemical molecules (compare H. Chick, A., 1908, ii, 314; 1910, ii, 990). G. B.

Poisoning by Nitrohalogenated Methanes. ANDRÉ MAYER, L. PLANTEFOL, and FRED. VLÈS (*Compt. rend.*, 1920, **171**, 1396—1397).—When gases of the type of chloropicrin, bromopicrin, and dichlorodinitromethane are inhaled, they act as irritants on the respiratory passages, but when they come in contact with the lungs, lesions are formed and a massive œdema, the fluid from which at the moment of death may form 58% of the total weight of the lung. In producing the latter effect, chloropicrin is the most powerful, bromopicrin and dichlorodinitromethane being eight to ten times less active. These substances are also toxic if injected intraperitoneally, the blood at the moment of death containing a considerable amount of methæmoglobin. W. G.

The Toxicity of the Chloromethyl Carbonates and Chloro-formates. ANDRÉ MAYER, H. MAGNE, and L. PLANTEFOL (*Compt. rend.*, 1921, **172**, 136—139).—The toxic effect of the different chloromethyl carbonates and chloroformates on rabbits,

guinea-pigs, and dogs was examined, the animals inhaling the vapours diluted with air. In the case of the chloromethyl carbonates, the successive introduction of chlorine atoms gives an increase in the toxicity of the substance up to the trichloro-stage. The introduction of a fourth chlorine atom diminishes the toxicity if the previous three chlorine atoms were all in one methyl group, but does not alter it if they were distributed between the two methyl groups. The introduction of two atoms of chlorine notably increases the toxicity. The most symmetrical distribution of the chlorine atoms gives the least toxicity.

The chloromethyl chloro-formates become more and more toxic as the number of chlorine atoms introduced increases. For the same number of chlorine atoms present in the molecule the chloroformates are more toxic than the carbonates. W. G.

Chemistry of Vegetable Physiology and Agriculture.

Acetaldehyde as an Intermediate Product in the Fermentation of Sugar by *Bacillus lactis aerogenes*. C. NEUBERG, F. F. NORD, and E. WOLFF (*Biochem. Zeitsch.*, 1920, **112**, 144—150).—Acetaldehyde has been established by the "fixation" method as an intermediate product in the fermentation of sugar by *B. lactis aerogenes*. S. S. Z.

Yeast Crops and the Factors which Determine them. ARTHUR SLATOR (T., 1921, **119**, 115—131).

[The Nature of] Yeast Fat. O. HINSBERG and E. ROOS (*Zeitsch. physiol. Chem.*, 1920, **111**, 304).—Polemical in reply to MacLean and Thomas (A., 1920, i, 652). The authors have already pointed out (*Zeitsch. physiol. Chem.*, 1904, **42**, 189) that the so-called pentadecenoic acid prepared by them was a mixture of much palmitic acid with another acid (probably stearic acid). They do not agree with MacLean and Thomas that the acid fraction from yeast fat, b. p. 130—150°, previously described by them, is a mixture of lauric acid, oleic acid, and linoleic acid. S. S. Z.

Antagonistic Action between Ions of Similar Charge. S. M. NEUSCHLOSS (*Kolloid Zeitsch.*, 1920, **27**, 292—306. Compare A., 1920, i, 698, 776).—It is shown that the surface tension of lecithin sols is increased by the presence of the chlorides of the alkalis, alkaline earths, and aluminium; the value increases with increasing salt concentration, and eventually passes through a maximum. These salts retard the inversion of sucrose by invertase, the amount of retardation increases with the concentration, and its

amount depends on the valency of the cation employed. The influence of the salts on fermentation is parallel with the degree of dispersion of the ferment solution. Both the above actions are in keeping with the adsorption isotherm, and it may be concluded that the retardation of fermentation by the presence of neutral salts is due to a reduction of the active ferment surface in the microheterogeneous system. When mixtures of the above-named salts are employed in any of the three reactions named, an antagonism is set up, inasmuch as the effects observed are dependent on the relative concentrations of the salts, but in no way dependent on the total salt concentration. The relative quantities in which the salts show the minimum antagonistic effect are determined by the valencies of the cations. The maximum antagonism in the case of equivalent cations occurs at the concentration ratio 1:1, whilst bivalent cations have the maximum effect at 1/20 the concentration of univalent cations and tervalent cations at 1/100 the concentration.

J. F. S.

The Susceptibility of the Fermentation of a Top Yeast to the Hydrogen-ion Concentration. H. von Euler and S. Heintze (*Zeitsch. physiol. Chem.*, 1919, **108**, 165—185).—The experiments were carried out with a strain of a top yeast (*SB* II) from Stockholms Södra Jästfabrik. It was found that the influence of the acidity on the rate of fermentation was dependent on the nitrogen content of the medium, and that the optimum hydrogen-ion concentration was about $P_H = 5$. In the case of weakly dissociated organic acids the quantity of the undissociated acid is great in relation to the concentration of the ions, and it also influences the course of fermentation. S. S. Z.

Alcoholic Fermentation. VIII. Influence of Zinc Chloride on the Alcoholic Fermentation of Living and Killed Yeast. S. Kostychev and L. Frey (*Zeitsch. physiol. Chem.*, 1920, **111**, 126—131).—Zinc chloride causes the formation of acetaldehyde in fermentation by hefanol and dried yeast, but not by living yeast; in addition a considerable part of the sugar is converted into unknown compounds. This production of acetaldehyde only occurs when sugar is present. In the case of autofermentation at the ordinary temperature, only traces of acetaldehyde can be established. S. S. Z.

Alcoholic Fermentation. IX. Influence of Cadmium and Zinc Salts on the Yeast Enzymes. S. Kostychev and S. Subkova (*Zeitsch. physiol. Chem.*, 1920, **111**, 132—140).—Cadmium salts alter to a very marked extent the normal course of fermentation. The best part of the sugar is converted into products of unknown composition, and acetaldehyde is produced at the same time. Proteolysis and, to a greater extent, reduction are inhibited by dilute solutions of cadmium salts, and the reduction of

acetaldehyde to alcohol is entirely stopped by small quantities of these salts. Acetaldehyde is produced, not only in the presence of oxygen, but also under anaerobic conditions. Cadmium salts do not cause the oxidation of ethyl alcohol to acetaldehyde. The action of cadmium and zinc salts is ionic. S. S. Z.

Enzyme Formation. ERICH KÖHLER (*Biochem. Zeitsch.*, 1920, **112**, 236—254).—The course of fermentation depends on the formation of a proenzyme of zymase and on the activation of the latter. Maltose is capable of activating zymase, whilst other sugars, such as dextrose, sucrose, and lævulose, have an inhibiting action as compared with it. On the other hand, in the production of the proenzyme, maltose wields an inhibiting influence in contradistinction to the other sugars. This explains the different physiological behaviour of a certain yeast to the various sugars. S. S. Z.

Phytochemical Reduction of Acetol with the Production of Optically Active Propylene Glycol. Presence and Utilisation of Racemic Substances in the Animal and Plant Organisms. E. FÄRBER, F. F. NORD, and C. NEUBERG (*Biochem. Zeitsch.*, 1920, **112**, 313—323).—Sugar was fermented by yeast in the presence of acetylcarbinol, the product of fermentation concentrated to a syrup, extracted with absolute alcohol, the alcohol extract evaporated, and extracted again with absolute alcohol. On the addition of ether, impurities were removed and the filtrate was concentrated, dissolved in absolute alcohol, and dried over sodium sulphate. *l*-Propylene glycol was obtained, b. p. 186—188°, $[\alpha]_D$ $-15{\cdot}66°$, $-16{\cdot}11°$, and $-7{\cdot}84°$, in alcohol. In aqueous solution $[\alpha]_D$ $-20{\cdot}48°$.

Top yeasts produced the reduction more readily than bottom yeasts. There appears to be no difference between substances of animal and plant origin as regards the question of asymmetry.

S. S. Z.

Alcoholic Fermentation. X. Fermentation is Life without Oxygen. S. KOSTYCHEV and PAUL ELIASBERG (*Zeitsch. physiol. Chem.*, 1920, **111**, 141—156).—Several species of mucor were employed for fermenting sugar under aerobic conditions, and the carbon dioxide produced through direct respiration was estimated. It was found that the organisms in the circumstances oxidised the sugar to an extent sufficient to cover their vital energy.

S. S. Z.

The Formation of Acetaldehyde in the Decomposition of Sugar by Moulds. CLARA COHEN (*Biochem. Zeitsch.*, 1920, **112**, 139—143).—Acetaldehyde was established as an intermediate product by means of the secondary sulphite "fixation" method in the fermentation of dextrose by *Aspergillus cellulosae*, *Monilia candida*, *Mucor racemosus*, *Mucor rouxii*, and *Oidium lactis*.

S. S. Z.

The Germicidal Value of some of the Chlorine Disinfectants. F. W. TILLEY (*J. Agric. Research*, 1920, **20**, 85—110).—A comparison of the germicidal value of "chloramin-*T*," sodium hypochlorite (Dakin's solution), hypochlorous acid (eusol), and chlorine in aqueous solution. Compared on a basis of weight of chloramin-*T* against weight of chlorine in the others, chloramin-*T* is the least efficient, but if the comparison is made on the basis of available chlorine contained, it is much more efficient against *Staphylococcus aureus*, much less efficient against *B. pyocyaneus*, and approximately equal in efficiency against *B. typhosus*. The experiments upon *B. tuberculosis* indicate that the chlorine disinfectants are of little value against this organism. There is thus a more or less "selective action" on the part of the various disinfectants.

Experiments on anthrax spores indicate that the germicidal action of chlorine compounds may extend over several days. The addition of ammonia to solutions of chlorine or hypochlorites very greatly increases their germicidal activity and tends to prevent depreciation in value on the addition of organic matter. W. G.

The Chemical Potential of Phenol in Solutions containing Salts, and the Toxicity of these Solutions towards Anthrax and *Staphylococcus*. J. STANLEY LAIRD (*J. Physical Chem.*, 1920, **24**, 664—672).—Determinations of the chemical potentials of phenol–sodium chloride solutions, using petroleum as immiscible solvent, confirm and extend the results obtained with toluene (A., 1920, i, 917). The abnormal results obtained by Lemon (*loc. cit.*) with 0·06% phenol are due to plasmolysis of the cocci. The increase or decrease of toxicity caused by adding ten different salts to 4% phenol solution is primarily due to change in chemical potential of the phenol. The increased toxicity caused by adding acetic acid required further study. J. R. P.

The Assimilation of Carbon Dioxide by Green Plants. P. MAZÉ (*Compt. rend.*, 1920, **171**, 1391—1393).—The author has collected leaves from a number of different kinds of trees and plants under the most varied atmospheric conditions and distilled them immediately without the addition of water under reduced pressure at 60°. In the distillate from almost all the species examined, he found ethyl alcohol, acetaldehyde, and nitrous acid, but he was never able to identify formaldehyde. In addition, the leaves of kidney beans and maize, collected in very fine weather, yielded acetylmethylcarbinol, the leaves of the elder yielded free hydrocyanic acid and glycollaldehyde, and poplar leaves gave lactaldehyde and a substance which on oxidation yielded propionic acid. The leaves of maize and kidney beans were free from acetylmethylcarbinol in the morning, but this substance appeared in increasing quantities as the day advanced on sunny days, but was entirely absent in wet, cold weather. The leaves of the kidney bean contained coumarin in the morning but not in the evening. W. G.

Preservation of Gentian Preparations Prepared from Dry, Unfermented Gentian Root. MARC BRIDEL (*J. Pharm. Chim.*, 1920, [vii], **22**, 411—418).—There was no change in the carbohydrate content of gentian powder, and of an extract prepared from it, when these were kept for nine years, but in the case of tinctures the quantity of carbohydrates decreased considerably during this period. The gentiopicrin decreased in the tinctures and disappeared entirely from the powder, but the latter still contained a quantity of hydrolysable glucoside. A tincture prepared with 60% alcohol, when kept for nine years, was found to be free from gentiopicrin, but to contain a glucoside, which appeared to be β-ethylglucoside. W. P. S.

Bio-chemistry of the Mahua Flower. GILBERT J. FOWLER, JAL D. EDAL BEHRAM, S. N. BHATE, K. HABIB HASSAN, S. MAHDIHASSAN, and N. N. INUGANTI (*J. Ind. Inst. Sci.*, 1920, **3**, 81—118). —Chemical and fermentation studies were made of the sugars in the mahua flower (*Bassia longifolia* and *B. latifolia*) with a view to its utilisation as a source of industrial alcohol. The total sugar content varies from 60—80%, and is greatest when the flowers are ready to fall. Yields of alcohol up to 90% of the theoretical were obtained by fermentation of a mash of the flowers with cultures of the natural yeast occurring in the flower. [See, further, *J. Soc. Chem. Ind.*, 1921, 22A.] G. F. M.

Composition of Inositol-phosphoric Acid of Plants. XVII. R. J. ANDERSON (*J. Biol. Chem.*, 1920, **44**, 429—438).—Data obtained from the analyses of carefully purified and recrystallised barium salts of the organic phosphorus compound of wheat bran are in close agreement with the calculated composition of barium salts of inositol-hexaphosphoric acid. The silver salts agreed with the formula $C_6H_6O_{24}P_6Ag_{12}$. The composition of phytic acid of plants, as determined from the analyses of salts of this acid, corresponds with inositol-hexaphosphoric acid, $C_6H_{18}O_{24}P_6$ or $C_6H_6O_6(PO[OH]_2)_6$. J. C. D.

Enzymes. IV. Emulsin, Cytase, Ereptase, and Urease in Germinating Barley. DARIO MAESTRINI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 164—166. Compare A., 1920, i, 273, 413). —When treated with 0·3% acetic acid solution, germinated barley yields an extract capable of hydrolysing amygdalin, the enzyme (emulsin) being found in the suspension of the meal as well as in the filtered extract. No enzyme capable of attacking the cellulose of the cellular membranes of young plants could be detected in germinated barley. The latter is also devoid of peptolytic enzymes and of enzymes able to decompose carbamide. T. H. P.

Organic Chemistry

The Absorption of Ethylene and Propylene by Sulphuric Acid. SYDNEY GLENN PRESTON PLANT and NEVIL VINCENT SIDGWICK (*J. Soc. Chem. Ind.*, 1921, **40**, 14—18T).—The authors have examined the influence of velocity of flow of the gas, purity of the gas, variation of temperature, and concentration of the acid on the absorption of ethylene by sulphuric acid. The results indicate that there are three successive stages in the absorption, namely, (1) the solution of ethylene in the liquid, (2) its reaction with sulphuric acid to give ethyl hydrogen sulphate, and (3) its reaction with ethyl hydrogen sulphate to give ethyl sulphate. Reaction (3) will proceed before the whole of the sulphuric acid has been converted into ethyl hydrogen sulphate, reactions (2) and (3) proceeding at rates which are proportional to the products of the concentration of ethylene and the concentrations of sulphuric acid and ethyl hydrogen sulphate respectively. Furthermore, ethyl hydrogen sulphate has a distinct autocatalytic effect.

Propylene is far more readily absorbed than is ethylene by sulphuric acid, but the reactions are more complex. In addition to the production of propyl hydrogen sulphate and propyl sulphate, a colourless oil separates which does not contain sulphur, and appears to consist of saturated compounds. It reacts with sodium, and is probably a mixture of open-chain secondary alcohols. The complexity of the molecule is of the order C_{12}. W. G.

Halogen Substitution Reactions. A. KRONSTEIN (*Ber.*, 1921, **54**, [*B*], 1—16).—The action of bromine in the presence of iron on a number of alkyl haloids has been investigated. Except in the case of *iso*pentane derivatives, it is found to be impossible to introduce more than one bromine atom at each carbon atom by this method, so that it appears that the action of bromine is both accelerated and restricted by the presence of iron. It is suggested that the primary action consists in the formation of iron haloid, which is able to bring about the elimination of halogen acid from the alkyl haloid if a halogen atom is not attached to the neighbouring carbon atom; addition of halogen then occurs subsequently: $CH_3{\cdot}CH_2Cl \xrightarrow{-HCl} CH_2{:}CH_2 \xrightarrow{+Br_2} CH_2Br{\cdot}CH_2Br$. If, however, the neighbouring carbon atom is attached to a halogen atom, the iron haloid protects it from further substitution. A similar accelerating and protective action must be ascribed to phosphorus in the Hell-Volhard-Zelinsky action, which invariably leads to α-monohalogeno-derivatives; it would appear, therefore, that this is not a case of simple substitution, and it is suggested that ketens are intermediately formed: $CH_3{\cdot}CH_2{\cdot}COCl \xrightarrow{-HCl} CH_3{\cdot}CH{:}CO \xrightarrow{+Br} CH_3{\cdot}CHBr{\cdot}COBr$.

Tribromohydrin, b. p. 218—222°, is formed exclusively by the action of molecular proportions of bromine and trimethylene bromide or propylene bromide in the presence of iron at 80°, or from the halogen (2 mols.) and *n*- or *iso*-propyl bromide (1 mol.).

The action of bromine on a mixture of $\beta\gamma$- and $\alpha\beta$-dibromobutanes leads to the formation of a mixture of isomeric tetrabromobutanes, which is transformed by an excess of bromine into $\alpha\beta\gamma\delta$-tetrabromobutane, colourless leaflets, m. p. 118°, and a tetrabromobutane, m. p. 39°. *iso*Butylene bromide is transformed by bromine at the ordinary temperature into iso*butylene tetrabromide*, colourless, heavy liquid, b. p. 169—171°/11 mm.

tert.-Amyl chloride is smoothly converted by bromine at the ordinary temperature in the presence or absence of iron into *$\beta\gamma$-dibromo-β-methylbutane*, b. p. 63—64°/15 mm., the constitution of which follows from its identity with the compound produced from β-methyl-Δ^{β}-butylene and bromine. With two molecular proportions of bromine, *tert.*-amyl chloride or bromide at 80°, and in the presence of iron, yields mainly *$\beta\gamma\gamma$-tribromo-β-methylbutane*, liquid, b. p. 119—120°/17 mm., together with small amounts of solid $\beta\gamma\delta$-tribromo-β-methylbutane; the latter, however, becomes the main product when the reaction is conducted very slowly and in such a manner that the temperature does not exceed 5°. Attempts to transform $\beta\gamma\delta$-tribromo-β-methylbutane into a symmetrical tetrabromo-derivative were unsuccessful, giving unchanged material and *$\alpha\beta\gamma\delta$-tetrabromo-β-bromomethylbutane*, $CBr(CH_2Br)_2\cdot CHBr\cdot CH_2Br$, monoclinic crystals, m. p. 115°, which is more readily prepared by the action of two molecular proportions of bromine on the tribromo-compound. Pentabromo*iso*pentane can be further brominated at 80°, yielding, successively, *$\alpha\beta\gamma\gamma\delta$-pentabromo-$\beta$-bromomethylbutane*, yellowish-white crystals, m. p. 90°, and *$\alpha\beta\gamma\gamma\delta\delta$-hexabromo-$\beta$-bromomethylbutane*, $CBr(CH_2Br)_2\cdot CBr_2\cdot CHBr_2$, pale yellow crystals, m. p. 174°; the latter substance does not react further with bromine in the presence of iron.

Primary *iso*amyl chloride exhibits a behaviour towards bromine and iron which differs markedly from that of the corresponding tertiary compound; with molecular proportions of the reagents, reaction is scarcely perceptible at 0°, whilst at 80° and in a sealed tube the violent reaction leads to the formation of much resinous matter; by the gradual addition of bromine to the chloride at 80°, it is found that about three-fourths of the original material remains unaffected, whilst the remainder is converted into *$\beta\gamma\gamma\delta$-tetrabromo-β-methylbutane*, pale yellow liquid, b. p. 148—150°/12 mm., the constitution of which is deduced from its smooth bromination to hexabromo*iso*pentane, m. p. 90°. Primary *iso*amyl chloride reacts with three molecular proportions of bromine at 0°, yielding unchanged chloride and $\alpha\beta\gamma\delta$-tetrabromo-β-bromomethylbutane.

The general results of the investigation indicate that bromination occurs at succeeding carbon atoms in an orderly manner; the bromination of $\beta\gamma$-dibromo-β-methylbutane, however, proceeds in an abnormal manner in so far as the liquid tribromo*iso*pentane is

concerned. Normal bromination might yield either of the compounds $CMe_2Br\cdot CHBr\cdot CH_2Br$ or $CH_2Br\cdot CMeBr\cdot CHBrMe$. The first formula undoubtedly represents the solid compound, whilst the liquid substance cannot be represented by the second, since, on further bromination, a hexabromo*iso*pentane instead of the expected pentabromo-compound is produced. The tribromo-derivative must therefore be unsymmetrical, and represented by the formula $CMe_2Br\cdot CBr_2Me$.

Methyl bromide, ethylene bromide, tribromohydrin, and $\alpha\beta\gamma\delta$-tetrabromobutane cannot be further brominated in the presence of iron; when heated for some days, they remain unchanged, whilst subsequently, with methyl bromide, for example, carbonisation sets in.

The observations recorded above enable an explanation to be given of the course of the bromination of 1:2-dichloro*cyclo*butane in the presence of iron (Willstätter and Bruce, A., 1907, i, 1018); the primary product is $\alpha\beta$-dichloro-$\alpha\delta$-dibromobutane, which, by loss of hydrogen chloride or bromide, and subsequent addition of bromine, yields $\alpha\beta$-dichloro-$\alpha\gamma\delta$-tribromobutane and α-chloro-$\alpha\beta\gamma\delta$-tetrabromobutane respectively. These substances are resistant to further bromination, since their carbon atoms are all united to halogen atoms. H. W.

Preparation of Ethyl Alcohol from Acetaldehyde. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P. 328342; from *Chem. Zentr.*, 1921, ii, 124).—Hydrogen is added to acetaldehyde by running the latter into the cathode chamber of an electrolytic cell charged with a suitable acid medium in such a manner that the concentration of acetaldehyde in the solution is maintained low. In these circumstances, the yield of alcohol is good, and the current efficiency is high. As the concentration of the aldehyde increases, the yield of alcohol falls continuously; at a concentration of 10%, the process appears, in general, to be uneconomical.

H. W.

Preparation of Alcohols of High Molecular Weight. GEORG SCHICHT A.-G. (D.R.-P. 327510; from *Chem. Zentr.*, 1921, ii, 124).—Solid or liquid alcohols of high molecular weight are prepared by reduction of more complex alkyl derivatives by treatment with aqueous alkali hydroxide solutions and alcohols. Thus, δ-*pentatriacontanol*, $C_{35}H_{71}\cdot OH$, m. p. 93—94°, is produced when stearyl ketone (2 molecules) is heated with sodium hydroxide solution (1 molecule) and alcohol (2 molecules) for three to six hours at 200—300°. The alcohols prepared from the ketones of the resin acids are viscous liquids. A small portion of the product of the reaction frequently becomes dehydrated, with formation of the corresponding ether or ethylenic compound. The aldehydes and peroxides, which, in addition to acids and alcohols, are formed by the incomplete oxidation of saturated hydrocarbons by air or oxygen, are converted into the corresponding alcohols by treatment

with aqueous-alcoholic alkali hydroxide solutions; this is particularly the case with the wax alcohols. H. W.

The Method of Pyrogenic Decomposition, at High Temperature, of Allyl Alcohol. (MLLE) EGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1921, [iv], **29**, 39—44).—When allyl alcohol is decomposed at high temperatures (see below), the two primary actions are $CH_2{:}CH{\cdot}CH_2{\cdot}OH = CH_2{:}CH{\cdot}CHO + H_2$ and

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH = CH_2{:}C{:}CH_2 + H_2O.$$

The acraldehyde obtained in the first reaction then undergoes further decomposition to give ethylene and carbon monoxide, whilst the allene in the second reaction unites with hydrogen to form propylene. Measurements show that of three molecules of propenol decomposed, two give acraldehyde and hydrogen and one gives propylene and water. Thus the principal decomposition is that which requires the least deformation of the molecule. W. G.

Preparation of Ethyl Nitrite. PAUL RENÉ DE WILDE and DAVEY BICKFORD SMITH & CIE (Schweiz. P. 86381; from *Chem. Zentr.*, 1921, ii, 124).—Sulphur dioxide is allowed to react with nitric acid in the presence of alcohol in accordance with the equation $EtOH + SO_2 + HNO_3 = H_2SO_4 + EtNO_2$. Forty-six grams of alcohol and 100 grams of nitric acid (D 1:38) yield 72 grams of ethyl nitrite. H. W.

Two Homologues of Ethylene Sulphide: αβ-Thiopropane and Thiobutane. MARCEL DELÉPINE and PIERRE JAFFEUX (*Compt. rend.*, 1921, **172**, 158—160).—*αβ-Thiopropane* and *αβ-thiobutane* were prepared by the action of sodium sulphide containing a little of the hydrogen sulphide on propylene chlorothiocyanate or dithiocyanate and on butylene bromothiocyanate or dithiocyanate. They are both colourless, mobile liquids. αβ-Thiopropane, $S{<}\begin{matrix}CH_2\\ |\\ CHMe\end{matrix}$, has b. p. 75—77°, D_4^0 0·964, n_D^{19} 1·473, and αβ-thiobutane, $S{<}\begin{matrix}CH_2\\ |\\ CHEt\end{matrix}$, has b. p. 104—105°, D_4 0·944, n_D^{15} 1·475. The b. p.'s and the densities of the αβ-thio-compounds in this series are lower than those of the corresponding αγ- or αδ-derivatives. These two sulphides are much more stable towards reagents than ethylene sulphide, and show no signs of polymerisation, even at the end of six months. W. G.

The Sudden Pyrogenic Decomposition of Formic Acid and the Preparation of Carbon Monoxide. J. A. MULLER and (MLLE) E. PEYTRAL (*Bull. Soc. chim.*, 1921, [iv], **29**, 34—39). —When formic acid is suddenly decomposed by passing it rapidly through a platinum tube at 1150°, the primary action is its decomposition into hydrogen and carbon dioxide. The production of carbon monoxide is a secondary action, due to the reduction of the

carbon dioxide by hydrogen. At a sufficiently high pressure, the velocity of this secondary action might become sufficiently high for it to appear that the formic acid was decomposing directly into carbon monoxide and water. W. G.

The Binary and Ternary Mixtures obtained in the Synthetic Manufacture of Acetic Acid. Paul Pascal, Dupuy, Ero, and M. Garnier (*Bull. Soc. chim.*, 1921, [iv], **29**, 9—21).—The two processes of manufacture considered are: (1) the direct oxidation of acetic acid and acetaldehyde; (2) the electrolytic oxidation of acetaldehyde or of paracetaldehyde in sulphuric acid solution. The densities and boiling points of binary mixtures of water–acetic acid, water–acetaldehyde, acetaldehyde–acetic acid, and of ternary mixtures of water–acetaldehyde–acetic acid are given, and graphs showing the variations are plotted. In the tables showing the boiling points, the composition of the liquid and the vapour are given in each case. The boiling points of ternary mixtures of acetic acid–sulphuric acid–water, and the composition of the liquid and vapour, are also given. W. G.

Synthetic Acetic Acid and Synthetic Acetone. Preparation of Acetic Acid, Acetates, and Acetone from Calcium Carbide. Production of Acetylene and its Catalytic Hydrogenation. Oxidation of Acetaldehyde to Acetic Acid. Acetone. J. T. Rooney (*Chem. and Met. Eng.*, 1920, **22**, 847—850; from *Chem. Zentr.*, 1921, ii, 123—124).—The synthesis depends on the four following reactions: (1) $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$; (2) $C_2H_2 + H_2O = CH_3{\cdot}CHO$; (3) $CH_3{\cdot}CHO + O = CH_3{\cdot}CO_2H$; (4) $2CH_3{\cdot}CO_2H = (CH_3)_2CO + CO_2 + H_2O$. The individual processes are described shortly. The synthesis was carried out on an extended scale during the war by the Canadian Electro Products Company at Montreal. H. W.

Catalytic Decomposition of the Chloroacetic Acids. J. B. Senderens (*Compt. rend.*, 1921, **172**, 155—158).—The organic acids undergo catalytic decomposition in the presence of catalysts, such as thorium oxide, to give the corresponding ketones (A., 1913, i, 342). The chloroacetic acids do not follow this rule. With thorium oxide or kaolin as catalysts at 220°, monochloroacetic acid gives hydrogen chloride, carbon dioxide and monoxide and carbon. In the case of trichloroacetic acid, the decomposition is more complex, there being three reactions, the first predominating: $CCl_3{\cdot}CO_2H = CHCl_3 + CO_2$;

$$2CCl_3{\cdot}CO_2H = C_2Cl_4 + 2HCl + 2CO_2;$$

$2CCl_3{\cdot}CO_2H = C_2Cl_6 + H_2O + CO_2 + CO$. In the presence of animal charcoal, monochloroacetic acid is decomposed, as recorded above. In the case of trichloroacetic acid, the change is almost entirely confined to the formation of chloroform. Chloral undergoes an entirely different decomposition in the presence of animal charcoal or thorium oxide. W. G.

The Oxidation of Acetoacetic Acid. N. O. ENGFELDT (*Zeitsch. physiol. Chem.*, 1921, **112**, 176—186).—On adding potassium permanganate to sodium acetoacetate, a vigorous reaction takes place. On filtering the products of the reaction, acetic acid and oxalic acid are contained in the filtrate, and glyoxylic acid also can be identified in it. It is assumed that at a certain stage of the oxidation process, the acetoacetic molecule is broken up, with the production of acetic acid and glyoxylic acid, the latter acid being eventually oxidised to oxalic acid. Hydroxybutyric acid does not react vigorously with potassium permanganate at the ordinary temperature, but, at the boiling temperature, acetone and carbon dioxide are formed if the reaction of the liquid is strongly acid. Oxalic acid and acetic acid are, on the other hand, produced when the reaction is weakly alkaline or neutral. It is assumed that acetoacetic acid is formed as an intermediate product in the oxidation of hydroxybutyric acid. S. S. Z.

An Occurrence of Fumaric Acid and of Inositol. L. ZECHMEISTER and P. SZÉCSI (*Ber.*, 1921, **54**, [*B*], 172—173). —A *potassium hydrogen fumarate*, $2C_4H_3O_4K,C_4H_4O_4$, has been isolated from the alcoholic extract of *Capsella bursa pastoris*, and identified by analysis and conversion into fumaric acid and its silver salt and methyl ester. *r*-Inositol, m. p. 218—219°, is obtained from the aqueous extract by a modified precipitation method with lead acetate; it is present to the extent of at least 0·03% of the dried drug. H. W.

Variation of the Rotatory Power of Tartaric Acid. R. DE MALLEMANN (*Compt. rend.*, 1921, **172**, 150—152).—A study of the effect of the chlorides and nitrates of the alkali and alkaline earth metals on the rotatory power of tartaric acid in aqueous solution (compare this vol., i, 7). For equal concentrations, the salts of the alkaline earth metals cause a greater depression in the rotatory power of tartaric acid than do the corresponding salts of the alkali metals. In the former series, the effect decreases in the order $Ca > Sr > Ba > Mg > Zn$. It is greater with the chlorides than with the nitrates or soluble sulphates. The effect increases with the concentration of the salt and of the tartaric acid, and also with the ratio salt/acid. Increase in temperature has the same effect as diluting the solution. The variation in the dispersion follows Darmois's rule (A., 1911, ii, 352). W. G.

Action of Hydrazine on Chloral Hydrate. GUSTAV KNÖPFER (*Monatsh.*, 1920, **41**, 455—466).—When treated with ferrous sulphate in presence of potassium hydroxide, the compound $C_9H_7ON_2Cl_3$ (I), formed when benzaldazine acts on excess of chloral hydrate, either fused or dissolved in glacial acetic acid, first loses hydrogen chloride, yielding the compound $C_9H_6ON_2Cl_2$ (II); the latter then takes up two atoms of hydrogen, giving the compound $C_9H_8ON_2Cl_2$ (III) (compare A., 1913, i, 703). The fact that compound III dissolves readily in alkali hydroxides in the cold and is reprecipitated by acids, that is, shows the same acid character

as compound I, renders it probable that the positions occupied by the two hydrogen atoms entering the molecule of II to give III are those of the hydrogen and chlorine atoms originally expelled from I.

If the bromo-compounds corresponding with the above chloro-compounds are indicated, respectively, by I′, II′, and III′ (A., 1916, i, 714), the action of benzaldazine on fused bromal hydrate gives I′, which is converted by potassium hydroxide into II′. On the other hand, in glacial acetic acid solution, the reaction yields a compound analogous in composition and properties with III, and identical with that obtained by reducing I′ by means of ferrous sulphate in presence of potassium hydroxide; this compound must then be III′ ($C_9H_8ON_2Br_2$). Further, compound III is formed by reduction of I in glacial acetic acid solution by means of hydrazine; since, also, III′ is formed in glacial acetic acid only when relatively large proportions of benzaldazine are used, mixtures of I′ and III′ being otherwise obtained, it is likely that the initial product is I′, and that this is reduced to III′ by the hydrazine liberated from the azine.

The behaviour of other aldazines towards chloral hydrate has been investigated, but only in the case of cuminaldazine were analysable products obtained, the reaction following the same course as that between benzaldazine and chloral hydrate. With other aldazines, the compounds of the three types I, II, and III, evidently formed simultaneously, could not be separated.

Ketazines act on chloral hydrate in the same way as free hydrazine, so that they are decomposed before they act. An exception to this behaviour is shown by the action of ketazines of the fatty series on chloral hydrate in aqueous solution at the ordinary temperature, one of the ketone residues being then replaced by one chloral hydrate residue: $CCl_3{\cdot}CH(OH)_2 + CR_1R_2{:}N{\cdot}N{:}CR_1R_2 = CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}N{:}CR_1R_2 + COR_1R_2$. The chloral-ketone hydrazones thus formed exhibit the greatest similarity to the simple chloral-hydrazine in appearance, behaviour, and instability; they have been already obtained by the action of carbonyl compounds on hydrazones (Curtius and Franzen, A., 1902, i, 831; Franzen and Eichler, A., 1910, i, 700).

From semioxamazide and chloral hydrate no definite product was obtained, but when chloral, instead of its hydrate, was triturated with the calculated amount of the azide, a quantitative yield of chloralsemioxamazone was formed: $CCl_3{\cdot}CHO + NH_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2 = CCl_3{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2 + H_2O$.

The *compound*, $C_{12}H_{13}ON_2Cl_3$, formed from cuminaldazine and chloral hydrate according to the equations

$$CCl_3{\cdot}CH(OH)_2 + (C_3H_7{\cdot}C_6H_4{\cdot}CH{:}N)_2 = C_3H_7{\cdot}C_6H_4{\cdot}CHO + CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}C_3H_7,$$

and the latter $-H_2 = C_{12}H_{13}ON_2Cl_3$, forms white crystals, m. p. 144°, and, when warmed with potassium hydroxide, is converted into the *compound*, $C_{12}H_{12}ON_2Cl_2$, which does not exhibit acid characters.

Chloralsemioxamazone, $C_4H_4O_2N_2Cl_3$, is a white compound which

exhibits no true melting point, but turns brown at 204° and decomposes completely at 227°.

*Chloral*iso*propylidenehydrazone*, $CCl_3\cdot CH(OH)\cdot NH\cdot N:CMe_2$, formed from chloral hydrate and dimethylketazine, is obtained in unstable, white crystals, m. p. 91°.

*Bromal*iso*propylidenehydrazone*, $CBr_3\cdot CH(OH)\cdot NH\cdot N:CMe_2$, has m. p. 80°.

*Chloral-β-*iso*butylidenehydrazone*, $CCl_3\cdot CH(OH)\cdot NH\cdot N:CMeEt$, forms crystals, m. p. 97°.

*Bromal-β-*iso*butylidenehydrazone*, $C_6H_{11}ON_2Br_3$, forms silky crystals, m. p. 80—81°. T. H. P.

Some Derivatives of Crotonaldehyde. CHARLES MOUREU, MARCEL MURAT, and LOUIS TAMPIER (*Bull. Soc. chim.*, 1921, [iv], **29**, 29—34).—Crotonaldehyde and hydrocyanic acid condense together in the presence of a trace of sodium hydroxide to give a cyanohydrin, $CHMe:CH\cdot CH(OH)\cdot CN$, b. p. 110—112°/12 mm., 119°/23 mm., 125°/36 mm., 131°/40 mm., 139°/70 mm., D_0^0 0·9813, D_4^{15} 0·9675, D_4^{21} 0·9633, n_D^{21} 1·4460. The cyanohydrin regenerates the aldehyde and hydrogen cyanide when heated above 115° at the ordinary pressure.

αβ-Dichlorobutaldehyde, $CHMeCl\cdot CHCl\cdot CHO$, b. p. 58—60°/12 mm., D_4^0 1·2915, D_4^{15} 1·2716, D_4^{21} 1·2666, n_D^{21} 1·4618, is obtained by passing dry chlorine into crotonaldehyde dissolved in carbon tetrachloride. When boiled with sodium acetate, this dichloroaldehyde loses hydrogen chloride, giving *α-chlorocrotonaldehyde*,

$$CHMe:CCl\cdot CHO,$$

b. p. 146—148° or 53—54°/20 mm., D_4^0 1·1598, D_4^{15} 1·4422, D_4^{23} 1·1404, n_D^{23} 1·478, which, on chlorination, gives crotonchloral [ααβ-trichlorobutaldehyde]. α-Chlorocrotonaldehyde gives a *cyanohydrin*, b. p. 137—138°/26 mm., D_4^0 1·2212, D_4^{15} 1·2007, D_4^{21} 1·1964, n_D^{21} 1·4762. W. G.

Disodium Phosphate as a Catalyst for the Quantitative Oxidation of Dextrose to Carbon Dioxide with Hydrogen Peroxide. EDGAR J. WITZEMANN (*J. Biol. Chem.*, 1920, **45**, 1—22). —The author confirms the observations of Löb on the accelerative effect of phosphate mixtures on the oxidation of dextrose with hydrogen peroxide (A., 1911, ii, 54, 504; 1913, i, 121). Dextrose may be quantitatively oxidised to carbon dioxide by hydrogen peroxide in the presence of the phosphate mixtures. The amount of the disodium phosphate used is the most significant factor in determining the reaction, and at 37° the phosphate mixture may be used repeatedly for the oxidation of additional amounts of dextrose, since the product of oxidation is removed. The mechanism of the reaction is discussed.

That compounds like hexose phosphate ester are the intermediates involved in the acceleration of oxidation described seems almost certain, but attempts to establish the formation of such a compound have failed.

There is experimental basis for the idea that the oxidation really

depends on the intermediate formation of a highly reactive perphosphate. In producing this accelerating effect on dextrose solutions, the disodium phosphate acts only as a peroxydase.

Dextrose is not oxidised by hydrogen peroxide in solutions containing sodium carbonate and hydrogen carbonate when these are used in the same molecular concentration as the two phosphates in the phosphate mixture. This indicates that available alkali is without appreciable influence on the oxidation of dextrose with hydrogen peroxide. J. C. D.

Preparation of Maltose. MAX FALCH (*Zeitsch. ges. Brauw.*, 1920, **43**, 281—283, 289—291, 297—299, 306—309; from *Chem. Zentr.*, 1920, iii, 880).—Attempts are described to prepare readily crystallisable maltose syrups by precipitation of dextrin with alcohol and barium hydroxide. The following procedure is recommended. Potato starch (300 grams) is mixed with water (1 litre) and malt extract, prepared from pale kiln or green malt by extraction during three hours (1 : 4; 30 c.c.), and added rapidly to 2 litres of boiling water. The mixture is cooled to 60°, treated with a further portion (30 c.c.) of malt extract, and maintained at 60° until two hours after it has ceased to give a reaction with iodine. It is then boiled, filtered, and so much water is added that the concentration sinks to D 1·04. Malt extract (240 c.c.) and hydrofluoric acid (7 mg. per 100 c.c. of liquid) are added, and the mixture is kept in corked flasks during three days at 30°; subsequently, the extract, which should not have become turbid, is treated with calcium carbonate, filtered, and boiled. The filtrate is concentrated in a vacuum until it contains 30% of water, seeded with a particle of maltose, and allowed to crystallise at 40°. If separation occurs only slowly, three portions of 90% alcohol (70 c.c.) are added on successive days; the crystals are filtered, and the residue is washed with 90% alcohol. One hundred grams of the dry product are dissolved in 30 c.c. of water on the water-bath, the solution is diluted with 90% alcohol (260 c.c.), heated to its boiling point, and filtered. Pure maltose separates from the cold solution after seeding, the yield being 30% of the air-dried starch. H. W.

The Constitution of the Disaccharides. V. Cellobiose (Cellose). WALTER NORMAN HAWORTH and EDMUND LANGLEY HIRST (T., 1921, **119**, 193—201).

The Synthesis of Sugars containing Sulphur and Selenium. FRITZ WREDE (*Zeitsch. physiol. Chem.*, 1920, **112**, 1—12).—*Dicellosyl selenide tetradeca-acetate*, $C_{52}H_{70}O_{34}Se$, was prepared by dissolving metallic potassium in alcohol, half saturating with dry hydrogen selenide in the absence of oxygen, and adding acetobromocellose to the boiling solution. Slender, almost colourless needles, m. p. 252°, were obtained, $[\alpha]_D^{18}$ $-47{\cdot}08°$ in chloroform. *Dicellosyl selenide*, $C_{24}H_{42}O_{20}Se$, was obtained from the

*h**

acetyl derivative by saponifying the methyl alcohol solution with ammonia and extracting it with ether. It is a yellow powder which decomposes at about 215°, $[\alpha]_D^{20}$ −85·93—86·35° in water. *Cellosyl-glucosyl sulphide hendeca-acetate*, $C_{40}H_{54}O_{26}S$, was prepared by suspending a mixture of acetobromocellose and acetobromoglucose in 96% alcohol, and treating it with potassium sulphide; it crystallises from methyl alcohol as dense, rhombic platelets, m. p. 163°, $[\alpha]_D^{18}$ −34·07° and −34·19° in chloroform. On treating the compound with *N*-sodium hydroxide, it was found that it contained eleven acetyl groups. *Cellosyl-glucosyl sulphide*, $C_{18}H_{32}O_{15}S$, was obtained from the acetyl derivative by treatment with ammonia; it decomposed at 160°, $[\alpha]_D^{14}$ −46·73° in water. The *potassium* salt, $C_{18}H_{30}O_{15}SK_2$, of the above compound was prepared by adding an alcoholic solution of potassium hydroxide to the alcoholic solution of the trisaccharide solution; it decomposed at about 180°. *Cellosyl-glucosyl selenide hendeca-acetate*, $C_{40}H_{54}O_{26}Se$, was prepared in a similar way to the sulphide; it crystallises in rhombic platelets combined in rosettes, m. p. 141°, $[\alpha]_D^{17}$ −39·76° and −40·36° in ethyl acetate. On hydrolysis with ammonia, the *cellosyl-glucosyl selenide*, $C_{18}H_{32}O_{15}Se$, was obtained as a yellow powder decomposing at about 160°. *Galactosyl-glucosyl selenide octa-acetate*, $C_{28}H_{38}O_{18}Se$, was prepared from acetobromoglucose and acetobromogalactose with potassium selenide in alcoholic solution, dense needles, m. p. 161°, $[\alpha]_D^{16}$ −30·99—30·72° in ethyl acetate. The compound was obtained from the acetyl derivative by hydrolysis with ammonia, $[\alpha]_D^{16}$ −48·35° in water. Dicellosyl sulphide was degraded by acid and by emulsin hydrolysis.

S. S. Z.

Starch, Starch Granules, and Starch Solutions. W. BIEDERMANN (*Pflüger's Archiv*, 1920, **183**, 168—196; from *Chem. Zentr.*, 1920, iii, 845).—Natural starch is a mixture of amylose (granulose or β-amylose), which gives a blue coloration with iodine and does not form a paste, and amylopectin, which is coloured violet by iodine and gelatinises when heated with water. Amylose is not actually soluble in hot water, but forms a hydrogel. The chief portion of it can be extracted from starch by water at 80°, and further quantities at 90°, but approximately amylose-free preparations can only be obtained with boiling water; these contain practically all the original amylopectin, together with a substance which gives a red to brown colour with iodine. By the action of saliva at 40°, the stromata can be rendered "achromatic," so that they are no longer coloured by iodine, and the material thus obtained is termed "amylocellulose." It is present in the starch granules of grain and leguminosæ in two forms: (1) as homogeneous, more or less swollen, fundamental matter of the stromata in intimate admixture with amylopectin, and (2) as individual, very highly refractive deposits (central particles). Solutions of amylopectin can be obtained from potato starch, but not from that of wheat or legumes. The stromata of potato and

arrowroot starch are rapidly and completely dissolved by treatment with saliva. These varieties of starch contain a type of amylopectin which, in the swollen condition, is very stable towards amyloses, but no amylocellulose. H. W.

New Formation of the Diastatic Ferment Outside the Living Cell. WERNER TESCHENDORF (*Fermentforsch.*, 1920, **4**, 184—190; from *Chem. Zentr.*, 1921, i, 131).—The degradation of starch to the achromatic point was not observed in experiments conducted in accordance with the recent directions of Biedermann (A., 1920, i, 15) unless the preparations were bacteriologically contaminated; the addition of saliva ash did not bring about this result. Re-examination of Schwiening's experiments (A., 1895, i, 125) did not show a spontaneous decomposition of starch in the presence of albumin when precautions were taken to ensure the freedom of the solutions from bacteria. H. W.

Wood Cellulose. F. LENZE, B. PLEUS, and J. MÜLLER (*J. pr. Chem.*, 1920, **101**, 213—264).—An account of comparative investigations of cotton and wood celluloses, with the ultimate object of discovering how far the latter is a suitable substitute for the former in its various applications. Contrary to the view previously held, the presence of wood gum (?) in the original material had no marked deleterious effect on the nitrocellulose obtained from it, although a difference was noticeable when the product was used for powder. The whole of the pentosans were removed from cotton by treatment with five parts of cold 17% sodium hydroxide solution for half an hour (Jentgen, *Kunststoffe*, 1911, 165), but subsequent extractions removed a constant quantity of material by a process the exact nature of which was not cleared up. Corresponding results were, however, only attained with mercerised cellulose after, respectively, two and six extractions, whilst sulphite cellulose was intermediate between the two in this respect. Further, of the residues undissolved by alkali, that from cotton alone gave a furfuraldehyde phloroglucide completely soluble in 80% alcohol, indicating that the others contained one or more xylose complexes more firmly attached to the cellulose molecule than those removed by alkali (compare Fromherz, *Diss.*, Strassburg, 1906; Schulze and Godet, A., 1909, ii, 824). Differentiation of the various forms of cellulose in various samples must be based on a determination of oxy- and hemi-celluloses, since the so-called β- and γ-celluloses (Cross and Bevan, "Researches on Cellulose," III [1905—1910], 22) prove to be merely mixtures of these, the former predominating in the first case, the latter in the second. This is achieved by estimation of the products of hydrolysis of hemicelluloses, consisting of mannose (Lindsey and Tollens, A., 1892, 802; Fromherz, *Diss.*, Freiburg, 1906, 29; Hägglund, A., 1915, i, 766; Klason, A., 1908, i, 717) and glucose, but not of galactose (compare Klason, *loc. cit.*; Lindsey and Tollens, *loc. cit.*) or lævulose (compare Krause, *Chem. Industrie*, 1906, **29**, 217; Koch, *Diss.*, Freiburg [Basle], 1909). Determinations of mannose (as

p-bromophenylhydrazone, by a process fully described) showed that whilst larger values were obtained from the alkaline extract than from the original material, extraction is only complete after a second treatment. Apparently, therefore, as in the case above, some mannose complexes are more firmly attached than others to the remainder of the molecule. Estimations of xylans by an improved process showed that there is no real correspondence between these and the proportion of wood gum, and confirmed the view that, whilst the furfuraldehyde obtained by hydrolysis is certainly derived in part from xylans, it is not entirely so. The proportion of oxycelluloses depends on the conditions employed in preparing cellulose, and they must therefore be produced in part during this treatment. Vieweg's acid number is untrustworthy (compare Schwalbe, "Chemie de Cellulose," 1918, 629), and Schwalbe's copper number is not accurate as a measure of these substances. This is, however, attained by hydrolysis of the hemicelluloses in the alkaline extract with 5% nitric acid (hydrochloric acid being unsuitable) and weighing the residual oxycellulose. The results obtained show the proportion of oxycelluloses to increase with the prolongation of any bleaching treatment. The original should be consulted for numerous analytical results obtained with cellulose prepared by various processes. J. K.

Action of Dilute Mineral Acids on Cellulose. A. Wohl and K. Blumrich (*Zeitsch. angew. Chem.*, 1921, **34**, 17—18).—From a study of the progressive changes in the cupric reducing power of the dissolved and undissolved fractions in the course of the prolonged heating of cotton cellulose with 0·3—5% hydrochloric acid at 100°, it is concluded that hydrolysis is accompanied by the formation of reversion products by interaction between reducing sugars in the solution and the undissolved residue. The insoluble residue (hydrocellulose) remaining after prolonged heating consists of such reversion products, which are more difficult to hydrolyse than the original cellulose. [See also *J. Soc. Chem. Ind.*, 1921, Mar.] J. H. L.

A New Method for the Production of Cellulose Acetate. W. Leigh Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 8—10T).—A trace of chlorine and a trace of sulphur dioxide, used together, form an excellent catalyst for the acetylation of cellulose by glacial acetic acid and acetic anhydride. By varying the conditions, a variety of pure esters may be obtained. If the temperature is kept below 65° and only a trace of sulphur dioxide is employed, the product is chiefly a diacetate, but if the ratio of chlorine to sulphur dioxide is nearer one, and particularly if the temperature is allowed to rise above 65°, the product is mainly cellulose triacetate.

For the analysis of cellulose acetates soluble in acetone, the simplest method is to dissolve a known weight of the acetate in acetone, shake the solution with a known volume of standard sodium hydroxide solution, allow the mixture to remain for

a day in a stoppered flask, and titrate the excess of alkali with standard acid, using phenolphthalein as an indicator. It is necessary to perform a blank estimation with a known weight of cellulose present. W. G.

New General Method of Preparation of Amines from Aldehydes or Ketones. GEORGES MIGNONAC (*Compt. rend.*, 1921, **172**, 223—226).—The aldehyde or ketone is dissolved in a solution of ammonia in absolute alcohol in equimolecular proportions. The solution is kept out of contact with air, finely divided nickel is added, and the mixture is vigorously shaken in an atmosphere of hydrogen at the ordinary temperature. When the absorption of hydrogen has ceased, the amine is isolated in the usual manner. This method has been successfully applied to a number of aldehydes and ketones. W. G.

Synthesis of Cyanic Acid by Oxidation of Formamide and Oxamic Acid. R. FOSSE (*Compt. rend.*, 1921, **172**, 160—162).—When formamide or oxamic acid is oxidised for a short time in ammoniacal solution with potassium permanganate, a liquid is obtained which gives no precipitate with xanthhydrol until it has been boiled for one hour with ammonium chloride. Further, the liquid obtained after the oxidation gives the typical colour reactions of cyanic acid. This compound is thus formed as an intermediate stage in the oxidation of these two amides to carbamide (compare Eppinger, A., 1905, i, 579). W. G.

Preparation of Anhydrous Hydrocyanic Acid. K. ZEIGLER (*Ber.*, 1921, **54**, [*B*], 110—112).—The following modification of Gattermann's process is described, in which potassium ferrocyanide is replaced by sodium cyanide; about a kilo. of the latter can be used at once, and the yield of acid is 90% of that theoretically possible, the cost being about one-fourth to one-third of that of the older process.

The apparatus consists of a glass flask of 5 litres capacity provided with a rubber stopper with three holes. The first of these serves for connexion with the Gattermann air condenser and apparatus; the second holds a dropping funnel, and the third the mercury safety tube, to which a second dropping funnel is attached by means of a side-tube. The ends of the dropping funnels are brought close together and immediately above a small funnel which is attached to the underside of the cork by means of a stout wire; the stem of the funnel is bent in the form of a **U**, and cut off so that the end is 0·5—1 cm. below the edge of the funnel. Concentrated sodium cyanide solution and equimolecular amounts of sulphuric acid (1 : 1) are allowed to flow into the funnel simultaneously; reaction occurs immediately and uniformly, and is practically complete in the funnel itself, so that fresh solutions are continuously brought into contact with one another whilst the bisulphate solution drips into the flask. After complete addition of the reagents, the remainder of the hydrocyanic acid is driven

into the receiver by heating the contents of the flask to the boiling point.

Anhydrous hydrocyanic acid can be preserved unchanged for months if sealed in a glass vessel with a little calcium chloride.

H. W.

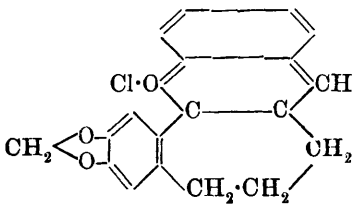
The Mode of Pyrogenic Decomposition, at High Temperature, of Benzene and Benzaldehyde. (MLLE) EGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1921, [iv], **29**, 44—47).—The principal reaction in the pyrogenic decomposition of benzene at high temperatures is that which gives rise to diphenyl and hydrogen. In the decomposition of benzaldehyde, the two primary reactions are $C_6H_5{\cdot}CHO = C_6H_6 + CO$ and $2C_6H_5{\cdot}CHO = C_{12}H_{10} + 2CO + H_2$. At the same time, a small amount of anthracene is formed, probably by the reduction of some of the benzaldehyde with hydrogen, and some methane results from the secondary decomposition of the diphenyl.

W. G.

Phenheptamethylene and certain other Compounds of the Phenheptamethylene Series. W. BORSCHE and A. ROTH (*Ber.*, 1921, **54**, [*B*], 174—177).—Benzosuberenone is reduced by amalgamated zinc and hydrochloric acid to *phenheptamethylene* [*benzosuberene*], $C_6H_4<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CH_2$, colourless, mobile liquid with an odour of petroleum, b. p. 217°/764 mm., which is stable towards permanganate. Similarly, methylenedioxybenzosuberenone (Borsche and Eberlein, A., 1914, i, 699) yields *methylenedioxybenzosuberene*, colourless crystals, m. p. 69—70°, b. p. 150—155°/15 mm.

Benzosuberenone condenses with benzaldehyde in the presence of alcoholic sodium ethoxide solution, with the formation of *benzylidenebenzosuberenone*, $C_6H_4<\begin{matrix}CO{\cdot}C(:CHPh)\\CH_2\text{———}CH_2\end{matrix}>CH_2$, needles, m. p. 82°, and is converted by *iso*amyl nitrite into *oximinobenzosuberenone*, small, yellow needles, m. p. 133—134°.

[With W. EBERLEIN.]—Methylenedioxybenzosuberenone is converted into *benzylidenemethylenedioxybenzosuberenone*, colourless, acute plates, m. p. 120—121°, *anisylidenemethylenedioxybenzosuberenone*, colourless needles, m. p. 159—160°, and *piperonylidenemethylenedioxybenzosuberenone*, yellow crystals, m. p. 184—185°. The *oxonium chloride* of o-*hydroxybenzylidenemethylenedioxybenzosuberenone* (annexed formula) is isolated as the double compound with ferric chloride, dark red leaflets, m. p. 159°, by the addition of solid ferric chloride to a solution of methylenedioxybenzosuberenone and salicylaldehyde in glacial acetic acid which has been saturated with hydrogen chloride.



H. W.

The Six Trichloronitrobenzenes and the Three Trinitrobenzenes; their Reaction with Sodium Methoxide. A. F. HOLLEMAN and F. E. VAN HAEFTEN (*Rec. trav. chim.*, 1921, **40**, 67—98).—Details are given for the preparation of the six trichloronitrobenzenes, and certain new compounds are described. When 3:4:5-trichloroacetanilide is nitrated in sulphuric acid solution, it gives 3:4:5-*trichloro*-2-*nitroacetanilide*, m. p. 177—178°, which, on hydrolysis, yields 3:4:5-trichloro-2-nitroaniline, m. p. 117°, from which 2:3:4-trichloro-1-nitrobenzene is readily obtained. When 2:5-dichloro-1:3-dinitrobenzene is reduced in alcoholic solution by titanous chloride, it gives 2:5-*dichloro*-3-*nitroaniline*, m. p. 122°, from which 2:3:5-trichloro-1-nitrobenzene is readily obtained.

When heated with an excess of sodium methoxide in methyl-alcoholic solution, 2:3:4-trichloronitrobenzene gives 5:6-dichloro-2-nitroanisole, m. p. 72·5°; 3:4:5-trichloronitrobenzene gives 2:6-dichloro-4-nitroanisole, m. p. 98°; 2:3:6-trichloronitrobenzene gives 3:4-dichloro-2-nitroanisole, m. p. 128° (compare Meldola and Eyre, T., 1902, **81**, 997), and 2:3:6-*trichloroanisole*, m. p. 42·8°; 2:4:5-trichloronitrobenzene gives 2:5-dichloro-4-nitroanisole, m. p. 101°; 2:3:5-trichloronitrobenzene gives 2:4-dichloro-6-nitroanisole, m. p. 44°; 2:4:6-trichloronitrobenzene gives 4:6-*dichloro*-2-*nitroanisole*, m. p. 72·5°. A quantitative study of these various reactions with sodium methoxide brings out the following points when the results are compared with those for other substances. The reaction constants at 0° are greatest for the chlorodinitrobenzenes, less for the trichloronitrobenzenes, still less for the dichloronitrobenzenes, and least of all for the chloronitrobenzenes. The chlorine atom which is displaced is always in an ortho- or para-position to the nitro-group, the greatest reaction constant for each group of isomerides being obtained when a chlorine atom para to the nitro-group is replaced. This mobility is further increased if a second chlorine atom is in an *ortho*- or *para*-position to the first one. None of the substituents in *s*-dichloronitrobenzene are rendered mobile with respect to sodium methoxide by the introduction of a third chlorine atom. For a particular group of isomerides, the velocity of substitution is lowest when the nitro-group is situated between two chlorine atoms *ortho* to it. In comparing the trichloronitrobenzenes against the dichlorodinitrobenzenes giving the same anisole derivatives, the two series cannot be arranged in the same order according to their velocity of reaction. Starting with the chloronitrobenzenes, passing to the trichloronitrobenzenes, the introduction of each successive chlorine atom increases the velocity constant thirteen to fourteen times.

A similar study was made with the three trinitrobenzenes. With sodium methoxide, 1:2:3-trinitrobenzene gives 2:6-dinitroanisole; 1:2:4-trinitrobenzene gives 2:4-dinitroanisole, and 1:3:5-trinitrobenzene gives 3:5-dinitroanisole. In the first two cases, the velocity of reaction at 0° was too great for it to be measured, but figures are given for 1:3:5-trinitrobenzene. W. G.

***o*-Chlorodinitrotoluenes. II.** GILBERT T. MORGAN and LESLIE AMIEL JONES (T., 1921, **119**, 187—192).

Preparation of *p*-Nitrotoluene-*o*-sulphonic Acid. WÄRITEOLLISUUS OSAKEYHTIÖ (D.R.-P. 327051; from *Chem. Zentr.*, 1921, ii, 125).—The product obtained by the sulphonation of *p*-cymene is directly treated at 40—60° with nitric acid, a mixture of nitric and sulphuric acids, or with nitrates. For technical purposes, the *p*-nitrotoluene-*o*-sulphonic acid thus produced is isolated as the sodium salt. H. W.

Auto-oxidation of α-Bromostyrene. CHARLES DUFRAISSE (*Compt. rend.*, 1921, **172**, 162—165).—α-Bromostyrene,

$CPhBr{:}CH_2$,

on exposure to air, readily undergoes oxidation, giving bromoacetophenone, $COPh{\cdot}CH_2Br$, the bromine thus migrating from the α- to the β-carbon atom. Similar changes have been noted for αα-dibromoethylene and α-chloro-α-bromoethylene. In general, the accumulation of electronegative groups on a double linking facilitates spontaneous oxidation of the compound, and this auto-oxidation is more marked if the groups are distributed in a dissymmetric manner. Of the three monobromostyrenes, only the α-bromostyrene oxidises spontaneously with any rapidity, and this is further proof of its constitution (this vol., i, 17). The ready formation of bromoacetophenone explains the lachrymatory action of α-bromostyrene after it has been kept for some time. W. G.

Hydrindene. I. W. BORSCHE and M. POMMER (*Ber.*, 1921, **54**, [*B*], 102—110).—The bromination, nitration, and sulphonation of hydrindene are described, as well as its behaviour in the Friedel-Crafts synthesis.

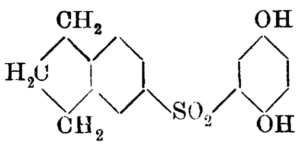
Hydrindene, b. p. 176°, D^{20} 0·9645, n_D 1·5381, is prepared by the catalytic hydrogenation of technical indene at the ordinary pressure in the presence of colloidal palladium and water.

The action of one, two, and four molecular proportions of bromine on the undiluted hydrindene in the presence of red phosphorus has been investigated, the addition of the halogen being effected gradually in diffused daylight, and the mixture subsequently heated until bromine vapours could not be any longer observed; the products in the first case are a monobromo-indene or -hydrindene, long, colourless needles, m. p. 125°, unchanged hydrindene, and indene; in the second they are the substance, m. p. 125°, and fractions of higher boiling point, from which an individual material could not be isolated, whilst in the third instance they are a *monobromohydrindene*, yellow liquid, b. p. 120—123°/diminished pressure, the substance, m. p. 125°, and a reddish-brown oil, which was not investigated further.

Nitrohydrindene, yellow liquid, b. p. 146°/12 mm., is most conveniently prepared by the gradual addition of nitric acid (D 1·52) to a solution of hydrindene in acetic anhydride in the presence of carbamide nitrate at −10°. It is smoothly reduced by hydrogen

and colloidal palladium to the corresponding *amine*, b. p. 241°. The experiments, however, have been discontinued for the time being, since oxidation with permanganate has shown the nitrohydrindene to be a mixture of the 4- and 5-forms, which, at present, cannot be separated from one another either before or after reduction.

Hydrindene resembles naphthalene in that it is converted by sulphuric acid into a mixture of the 4- and 5-monosulphonic acids, the proportion of the latter increasing with rise of temperature. Pure sodium hydrindene-5-monosulphonate is conveniently obtained by the action of concentrated sulphuric acid on the hydrocarbon at 150°, neutralisation of the product, and addition of sodium chloride. The following derivatives are obtained by the usual methods: hydrindene-5-sulphonyl chloride, colourless prisms, m. p. 40°; sulphonamide, m. p. 134·5°; *anilide*, colourless needles, m. p. 129°; p-*toluidide*, m. p. 143—144°; *sulphinic acid*, m. p. 71—72°, and, from it, *quinol-5-hydrindenesulphone* (annexed formula), colourless crystals, which become brown when exposed to air, m. p. 200—201°; 5-*thiolhydrindene*, yellow oil, which solidifies when cooled, b. p. 254—255°/754 mm.; 5:5′(?)-*dihydrindylsulphone*, greenish-yellow crystals, m. p. 180—181°. The *nitrile* of hydrindene-5-carboxylic acid, b. p. 105°/15 mm., is only obtained in small amount by the distillation of sodium hydrindene-5-sulphonate with potassium cyanide (the main product is hydrindene), but can be prepared from cyanogen bromide and hydrindene.



Acetylhydrindene, $C_9H_9 \cdot COMe$, b. p. 267—268°/748 mm. (compare von Braun, Kirschbaum, and Schuhmann, A., 1920, i, 618), is obtained by the action of acetyl and aluminium chlorides on a solution of hydrindene in carbon disulphide at 0°, and is shown to be a mixture of the 4- and 5-derivatives, since, on oxidation, it yields a mixture of benzene-1:2:4- and -1:2:3-tricarboxylic acids; the derivatives which are described, however, appear to belong to the 5-series, since the physical constants agree with those given by von Braun and his co-workers, so that it would seem that the 4-isomerides are either eliminated during the process of purification or, on account of steric hindrance, are not formed. The following compounds are described: hydrindene-5-carboxylic acid, m. p. 183°; acetylhydrindenesemicarbazone, m. p. 230—231°; acetylhydrindeneoxime, colourless prisms, m. p. 119°, which, when subjected to the Beckmann transformation, gives 5-*acetylaminohydrindene*, from which the corresponding *amine*, colourless oil, b. p. 247°/atmospheric pressure, m. p. 33—34°, is obtained; 5-hydrindyl bromomethyl ketone, m. p. 61°; 5-*hydrindyl anilinomethyl ketone*, $C_9H_9 \cdot CO \cdot CH_2 \cdot NHPh$, needles, m. p. 134°; p-*methoxycinnamoylhydrindene*, $C_9H_9 \cdot CO \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$, m. p. 92—93°.

A mixture of 4- and 5-*benzoylhydrindenes*, m. p. above 40°, is similarly obtained from the hydrocarbon, benzoyl chloride, and

aluminium chloride. It yields an *oxime*, m. p. 153—154°, which is converted by the Beckmann transformation into the *anilide* of hydrindene-5-carboxylic acid, colourless needles, m. p. 126°. 5-*Benzoylaminohydrindene*, long, colourless needles, has m. p. 137°. H. W.

Δ^1-Dihydronaphthalene. III. Modes of Formation of Δ^1-Dihydronaphthalene. FRITZ STRAUS and LEO LEMMEL (*Ber.*, 1921, **54**, [*B*], 25—40).—Δ^1-Dihydronaphthalene has been obtained previously by Straus and Lemmel (A., 1913, i, 256) by the protracted action of a 5% solution of sodium ethoxide on Δ^2-dihydronaphthalene at 140°. The same substance was shortly afterwards isolated by Willstätter and King (A., 1913, i, 353), who, however, considered their product to be the Δ^2-isomeride (compare Straus, A., 1913, i, 455). The further investigation of the relationships between naphthalene, Δ^1- and Δ^2-dihydronaphthalene, and tetrahydronaphthalene necessitated the discovery of a method which would allow the approximate estimation of the Δ^1- and Δ^2-dihydro-compounds in a mixture of the four substances, and, for this purpose, mercuric acetate is found to be a suitable reagent. Naphthalene and tetrahydronaphthalene remain unaffected by it, whilst Δ^2-dihydronaphthalene is converted into an additive product, which is soluble in hot benzene, and Δ^1-dihydronaphthalene is oxidised, with the formation of mercurous acetate,

$$C_{10}H_{10} + 2(CH_3{\cdot}CO_2)_2Hg + 2H_2O = C_{10}H_{10}(OH)_2 + 2CH_3{\cdot}CO_2Hg + 2CH_3{\cdot}CO_2H.$$

The difference in the behaviour of the two dihydro-derivatives corresponds exactly with that of allyl- and propenyl-benzenes. Further examination of the isomerisation of Δ^2-dihydronaphthalene under the influence of alcoholic ethoxide solution has shown that the displacement of the double bond takes place with greater readiness than was formerly supposed; for each concentration of alkyloxide, however, a minimal temperature is necessary to effect noticeable isomerisation. In the reduction of naphthalene by sodium and ethyl alcohol according to the method of Bamberger and Lodter (A., 1888, 292; 1896, i, 96), the hydrocarbons produced are ultimately subjected to the action of boiling 7·5% ethoxide solution, under which conditions slow isomerisation of the Δ^2-derivative probably occurs, whilst during the solution of the sodium it is certain that the local concentration of the ethoxide considerably exceeds this amount. The crude dihydronaphthalene therefore invariably contains the Δ^1-isomeride, probably to the extent of about 5%, but this does not represent the total quantity formed, since, under the experimental conditions, the tetrahydronaphthalene which is present can only result from the reduction of the Δ^1-derivative. The preparation of the latter can now, however, be greatly simplified, since, after completion of the reduction of naphthalene by sodium and ethyl alcohol according to Bamberger and Lodter, it is only necessary to distil off a portion of the solvent, and thus increase the concentration of the ethoxide solu-

tion in order to bring about the complete conversion of the Δ^2- into the Δ^1-derivative. The separation of the latter from naphthalene and tetrahydronaphthalene is effected by converting it into the dibromide, from which the hydrocarbon is readily regenerated.

The further reduction of the dihydro- to tetrahydro-naphthalene is effected by hydrogen in alcoholic solution in the presence of palladium. This procedure possesses the advantage over the use of platinum and glacial acetic acid that the reaction ceases after the absorption of a molecule of the gas, and that the second nucleus is absolutely unaffected; differences in the rate of absorption of hydrogen by the Δ^1- and Δ^2-isomerides could not be detected.

The preparation of dihydronaphthalene by the elimination of hydrogen chloride from β-chlorotetrahydronaphthalene at 190—200°, of water from *ac*-tetrahydro-β-naphthol by potassium hydroxide, and by the decomposition by heat of *ac*-tetrahydro-β-naphthylamine nitrite has been repeated; in every case it is shown that Δ^1-dihydronaphthalene is the sole product, and not the Δ^2-derivative, as has been previously supposed, the error being due to the remarkably close proximity of the melting points of the dibromides. It has been indicated previously (*loc. cit.*) that Willstätter and King's product, obtained by distilling the quaternary hydroxide of tetrahydro-β-naphthylamine in a vacuum, is also the Δ^1-derivative, and it is now shown that its production cannot be ascribed to the primary formation of the Δ^2-isomeride and conversion of the latter into the Δ^1-compound under the influence of the trimethylamine simultaneously produced.

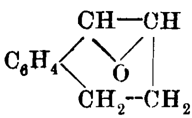
Δ^1-Dihydronaphthalene is also produced by the distillation of potassium Δ^1-dihydronaphthoate with slaked lime; a *substance*, $C_{20}H_{20}$, large, yellow leaflets with blue fluorescence, m. p. 97·5—100°, which appears to be formed by the polymerisation of two molecules of dihydronaphthalene, is also formed. H. W.

Δ^1-Dihydronaphthalene. IV. Conversion of Δ^1-Dihydronaphthalene into Alicyclic Substitution Products of Tetrahydronaphthalene. FRITZ STRAUS and AUGUST ROHRBACKER [and, in part, LEO LEMMEL] (*Ber.*, 1921, **54**, [*B*], 40—69).—The preparation and properties of a series of additive compounds of Δ^1-dihydronaphthalene have been investigated with the object of comparing the behaviour of these and the similar compounds of Δ^2-dihydronaphthalene with those formed from allyl and propenyl benzenes.

1-*Bromo*-Δ^1-*dihydronaphthalene*, $C_6H_4<\begin{matrix}CBr:CH\\CH_2\cdot CH_2\end{matrix}$, colourless liquid, which darkens when preserved, b. p. 144—146°/17 mm., is most readily obtained by heating 1:2-dibromotetrahydronaphthalene under diminished pressure at 130°, and finally at 175°; small amounts of naphthalene and Δ^1-dihydronaphthalene are obtained as by-products, the occurrence of the former being very difficult to explain. 2-*Bromo*-1-*methoxytetrahydro*-

naphthalene, $C_6H_4<\begin{matrix}CH(OMe)\cdot CHBr \\ CH_2\text{———}CH_2\end{matrix}$, liquid, b. p. 154—156°/13 mm., is the sole product of the action of boiling methyl alcohol in the presence of magnesium carbonate on 1 : 2-dibromotetrahydronaphthalene, and the main product (in addition to some naphthalene and [?] monobromodihydronaphthalene) when sodium methoxide solution is used.

Δ^1-Dihydronaphthalene is converted by hypochlorous acid into 2-*chloro*-1-*hydroxytetrahydronaphthalene* (Δ^1-*dihydronaphthalene chlorohydrin*), coarse, transparent needles, m. p. 92°. The corresponding *bromohydrin* is most readily produced by warming a solution of 1 : 2-dibromotetrahydronaphthalene in aqueous acetone in the presence of magnesium carbonate; it forms long, transparent needles, m. p. 111—112°, and is converted by dry hydrogen bromide into 1 : 2-dibromotetrahydronaphthalene, and reduced by zinc dust and alcohol or amalgamated aluminium and ether to Δ^1-dihydronaphthalene. Considerable difficulty is encountered in allocating the positions of the substituents in the bromohydrin, since both are readily removed simultaneously; the bromohydrin is transformed by sodium in moist ethereal solution into a mixture of Δ^1-dihydronaphthalene and tetrahydro-β-naphthol, b. p. 139—140°/12 mm. (the latter is most conveniently identified as the *phenylurethane*, pearly leaflets, m. p. 98—99°, which decomposes at 185—200°, giving carbon dioxide and pure Δ^1-dihydronaphthalene), but the reaction is devoid of theoretical significance, since the ethylene oxide (annexed formula) is intermediately formed (see later). The constitution of the bromohydrin is, however, placed beyond doubt by the following series of changes: the substance is oxidised by sodium dichromate and dilute sulphuric acid to 2-*bromo*-1-*ketotetrahydronaphthalene*, pale yellow oil with a characteristic, extremely unpleasant odour, b. p. 140—142°/0·5—1 mm. (*oxime*, colourless needles, m. p. 136·5—137°), which is reduced by zinc dust and alcohol to 1-*ketotetrahydronaphthalene*, b. p. 132—133°/13 mm. (*oxime*, m. p. 103°). The latter is converted by sodium in boiling absolute alcoholic solution into tetrahydro-α-naphthol, b. p. 132—134°/12—13 mm., the *phenylurethane* of which crystallises in short needles, m. p. 121—122°, and is decomposed quantitatively when heated into carbon dioxide, aniline, and Δ^1-dihydronaphthalene.



Δ^1-*Dihydronaphthalene oxide* is obtained by the gradual addition of the calculated amount of methyl-alcoholic potassium hydroxide solution to an ice-cold solution of the bromohydrin in absolute alcohol; it forms a transparent, mobile liquid with a pronounced odour of naphthalene, b. p. 86—88°/1—2 mm., 76—78°/0 mm., which readily polymerises to a colourless resin when distilled in the vacuum of a water-pump; it has m. p. 20—21°. It is converted by hydrogen bromide in glacial acetic acid solution into 2-bromo-1-hydroxytetrahydronaphthalene, by sodium and moist

ether into *ac*-tetrahydro-β-naphthol, and by piperidine into 1-*hydroxy*-2-*piperidinotetrahydronaphthalene*,

$$C_6H_4<\begin{matrix}CH(OH)\cdot CH\cdot C_5NH_{10} \\ CH_2\text{------}CH_2\end{matrix},$$

m. p. 72—73°. The intramolecular transformation of the oxide into β-ketotetrahydronaphthalene does not take place very smoothly, since polymerisation frequently occurs under conditions which would otherwise be suitable (such as boiling with bisulphite or aqueous acids). The change is best accomplished by passing dry hydrogen chloride into the solution of the oxide in light petroleum. The yield of pure ketone, after purification through the bisulphite compound, amounts to 50—60%, but the by-products have not been investigated. The substance has b. p. 136—137°/22 mm., m. p. 17—18° (oxime, needles, m. p. 86·5—87·5°; phenylhydrazone, shining leaflets, m. p. 107°), and thus agrees in its properties with the product obtained by Bamberger and Lodter by the action of quinoline on 3-chloro-2-hydroxytetrahydronaphthalene. The latter method, with the exception that pyridine has been substituted for quinoline, has been applied directly to 2-bromo-1-hydroxytetrahydronaphthalene, a mixture of the two ketotetrahydronaphthalenes being thereby produced (in which the α-isomeride is in excess), which can be separated readily by taking advantage of the differing behaviour of the components towards bisulphite. The formula of the β-ketone does not appear to afford a ready explanation of the instability of the substance and its derivatives, or, in particular, of its ready autoxidisability in alkaline solution to dark indigo-blue solutions.

2-Bromo-1-hydroxytetrahydronaphthalene is transformed by piperidine into 1-hydroxy-2-piperidinotetrahydronaphthalene, m. p. 73—74° (see above), which yields a *hydrochloride*, rods, m. p. 182—183°, an *aurichloride*, long, yellow needles, m. p. 167—168° (decomp.), a *platinichloride*, small needles, m. p. 186—188° (decomp.), and a *picrate*, long, yellow rods, m. p. 147·5—148·5°. The *benzoyl* derivative has m. p. 81° (*hydrochloride*, slender, colourless needles, m. p. 176·5—177·5°). 2-*Diethylamino*-1-*hydroxytetrahydronaphthalene* is a colourless, rather viscous liquid, b. p. 166—167°/12—13 mm., the *hydrochloride* of which could not be caused to crystallise. 2-*Dimethylamino*-1-*hydroxytetrahydronaphthalene* has b. p. 170—171°/20 mm., and solidifies at the laboratory temperature (*hydrochloride*, prismatic needles, m. p. 173—175°). 2-*Methylamino*-1-*hydroxytetrahydronaphthalene* is a colourless, viscous oil, b. p. 164—166°/12—13 mm. (*hydrochloride*, m. p. 183—184° after softening at 179°).

The preparation of the stereoisomeric 1:2-*dihydroxytetrahydronaphthalenes* is effected according to the directions of Leroux (A., 1909, i, 299) for the corresponding 2:3-glycols; the *cis-trans*-modification, long, colourless needles, m. p. 112—113° (*acetate*, transparent, pointed prisms, m. p. 84°, which quantitatively regenerates the glycol when hydrolysed with methyl-alcoholic potassium hydroxide solution), is obtained by the action of aqueous

alkali on the bromohydrin, the ethylene oxide being probably formed intermediately. A mixture of the acetates of the two forms is produced by the action of potassium acetate and glacial acetic acid on 1:2-dibromotetrahydronaphthalene, which could not be caused to crystallise, even after being distilled; on hydrolysis, a mixture of glycols is formed; this is again converted into the mixed acetates, which now slowly solidify. Separation of them is ultimately effected mechanically after crystallisation from light petroleum. cis-cis-1:2-*Dihydroxytetrahydronaphthalene acetate* forms large, colourless, coarse prisms, m. p. 78·6—79·2°, whilst the corresponding glycol crystallises in leaflets, m. p. 101·5—102°. The configuration assigned to the glycols depends on the observation that the isomeride of lower melting point is formed exclusively by the oxidation of Δ^1-dihydronaphthalene with potassium permanganate. This is in contrast with the formulation adopted by Leroux, who considers that the *cis-cis*-modifications are invariably formed from the bromohydrins. The action of mercuric acetate on Δ^1-dihydronaphthalene (compare preceding abstract) gives a mixture of the stereoisomeric glycols.

Oxidation of *cis-trans*-1:2-dihydroxytetrahydronaphthalene by potassium permanganate gives *o*-carboxyhydrocinnamic acid, m. p. 165·5—167°. H. W.

Formation of Salts of Dicarboxylic Acids with Aniline and its Homologues. TH. SABALITSCHKA and M. DANIEL (*Ber. Deut. pharm. Ges.*, 1920, **30**, 481—483).—The normal salts of certain dibasic acids with aniline or its homologues, if, indeed, they exist at all, are decomposed in aqueous solution into the acid salt and free base. Even when the acid and base are dissolved in water in equivalent proportions, it is the acid salt which crystallises out, as instanced by the case of aniline with succinic, maleic, and fumaric acids, whilst with the homologues of aniline the acids in question actually will not dissolve the bases in the proportion theoretically required for the formation of a normal salt. G. F. M.

D.M. (Diphenylamine Arsenious Chloride). A. CONTARDI (*Giorn. Chim. Appl.*, 1920, **1**, 11—26).—It has been shown by Merz and Weith (A., 1880, 813) that only traces of diphenylamine are formed when the double compound of aniline and zinc chloride, $ZnCl_2,2NH_2Ph$, is heated in an open vessel, even at a high temperature. The author finds, however, that when the double compound of aniline hydrochloride and zinc chloride, $ZnCl_2,2NH_2Ph,HCl$ (1 mol.), is heated with aniline (2 mols.), ammonia is liberated and diphenylamine formed. The reactions taking place appear to be:

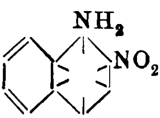
$$ZnCl_2,2(NH_2Ph,HCl) + 2NH_2Ph = 2NH_4Cl + NHPh_2 + ZnCl_2,2NH_2Ph$$

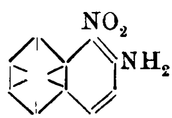
and $ZnCl_2,2NH_2Ph + 2NH_4Cl = 2NH_3 + ZnCl_2,2(NH_2Ph,HCl)$. The preliminary preparation of aniline hydrochloride is, indeed, found to be unnecessary, addition of zinc and ammonium chlorides to

heated aniline yielding diphenylamine; after a small quantity of zinc chloride has been added and the reaction started, a mixture of zinc oxide and ammonium chloride may then be introduced. Successive additions of aniline may be made, and the residual mass fractionally distilled in a vacuum. A yield of 90% of diphenylamine is obtainable.

For the preparation of diphenylaminearsenious chloride, $NH{<}^{C_6H_4}_{C_6H_4}{>}AsCl$ (?), known as D.M. or *adamsite*, fused diphenylamine (1 mol.) is treated with hydrochloric acid (D 1·18) (1·1 mols.), the mass heated and stirred until almost free from water, and the hydrochloride (2 mols.), either moist or after further drying in a desiccator at 50—60°, mixed with arsenic trioxide (1 mol.) and fused in a covered vessel provided with a wide efflux tube; when fusion has been maintained for four hours, the temperature rises to 200°, and the reaction is finished, a yield of 95% being obtained. T. H. P.

Action of *o*-Chlorobenzaldehyde on Feebly Basic Amines, particularly those of the Naphthalene Series. Constitution of Derivatives of Naphthalene. FRITZ MAYER and AUGUST BANSA (*Ber.*, 1921, **54**, [*B*], 16—24).—It has been shown previously (Kalischer and Mayer, A., 1916, i, 843; Mayer and Stein, A., 1918, i, 36) that the action of *o*-chlorobenzaldehyde on feebly basic amines can frequently be so regulated that iminoaldehydes are formed in place of the usual azomethines. The behaviour of the nitronaphthylamines is now described (compare Mayer and Levis, A., 1920, i, 31). 2-Nitro-*α*-naphthylamine appears to yield small quantities of the corresponding iminoaldehyde, although the product could not be isolated with certainty or converted into the corresponding naphthacridine in substance; azomethines are formed from 5- and 8-nitro-*α*-naphthylamines and from 5-nitro-*β*-naphthylamine, but 2:4-dinitro-*α*-naphthylamine could not be caused to react. As far as the chief compounds are concerned, these results appear to be normal, since the measurement of the electrical conductivity of the bases, and observations of the stability of their hydrochlorides, show that 1-nitro-*β*-naphthylamine is a stronger base than 2-nitro-*α*-naphthylamine. The difference is explicable on the basis of Harries' formula for naphthalene (compare Willstätter and Waser, A., 1912, i, 18), according to which 2-nitro-*α*-naphthylamine (I) is an aromatic amine united to an olefinic ring, in which the basicity of the amino-group is depressed by its proximity to the nitro-group, whilst 1-nitro-*β*-naphthylamine contains the basic group in the olefinic portion of the molecule, its function being consequently more marked and less influenced by the negative group.

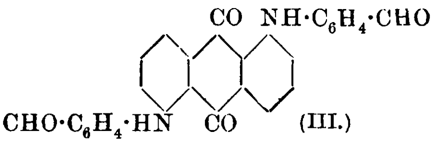

(I.)


(II.)

The action of *o*-chlorobenzaldehyde on aminophenols has also

been investigated, and a further extension of the field is opened up by the observation that *o*-chloroacetophenones react with feebly basic amines.

For the preparation of azomethines, the components are heated for half an hour on the water-bath, frequently after addition of a little alcohol. The abnormal condensation, leading to the formation of iminoaldehydes or acridines, is effected by heating the amine with an excess of freshly distilled *o*-chlorobenzaldehyde in the presence of naphthalene or nitrobenzene, anhydrous sodium carbonate, and copper powder at 220°. The following individual compounds are described: o-*chlorobenzylidene*-5-*nitro*-α-*naphthylamine*, $NO_2\cdot C_{10}H_6\cdot N:CH\cdot C_6H_4Cl$, m. p. 180°; o-*chlorobenzylidene*-8-*nitro*-α-*naphthylamine*, dark yellow, rhombic prisms, m. p. 122°; o-*chlorobenzylidene*-5-*nitro*-β-*naphthylamine*, greenish-yellow, hair-like crystals, m. p. 164°; o-*hydroxyphenyl*-o-*chlorobenzylidene-amine*, slender needles, m. p. 93°.



(III.)

2:4-Dinitroaniline and *m*-chlorobenzaldehyde yield m-2 : 4-*dinitrophenylaminobenzaldehyde*, m. p. 129°, which, however, could not be completely freed from the original amine. *p*-Chlorobenzaldehyde does not react with 2:4-dinitroaniline. *o*-Chlorobenzaldehyde and 1:5-diaminoanthraquinone yield oo′-(1 : 5 - *anthraquinonyldi-imino*)*dibenzaldehyde* (III). H. W.

Preparation of Carboxylic Acids of Carbocyclic and Heterocyclic Compounds. KARL W. ROSENMUND and ERICH STRUCK (D.R.-P. 327049; from *Chem. Zentr.*, 1921, ii, 73—74).—Halogenated derivatives of carbocyclic or heterocyclic compounds are caused to react with cyanides in an aqueous medium in the presence of copper or copper compounds. The process may be applied to heterocyclic compounds as well as to halogenated derivatives of benzene, naphthalene, anthracene, or other substances containing a benzenoid nucleus. The presence of other substituents in addition to halogen does not affect the reaction. In those cases in which difficulty is encountered owing to the insolubility of the compound in an aqueous medium, a solvent such as alcohol or pyridine may be added with advantage. In one case only (action of potassium cyanide on chloronitrobenzene) was the formation of notable amounts of nitroaniline in addition to nitrobenzoic acid observed; in all other instances the corresponding carboxylic acid was obtained in very good yield. The preparation of the following substances is particularly described: Benzoic acid by treatment of chlorobenzene with potassium and cuprous cyanides in alcohol (25%) at 210°; phthalic acid from *o*-dibromobenzene; anthranilic and α-naphthoic acids from *o*-bromoaniline and α-bromonaphthalene respectively. Thiophen-2-carboxylic acid is obtained from 2-bromothiophen, potassium cyanide, and a little finely divided copper in aqueous pyridine at 200°. H. W.

Preparation of Perhydrophenylnaphthylmethane-*o*-carboxylic Acid. RICHARD WILLSTÄTTER (D.R.-P. 325714; from *Chem. Zentr.*, 1920, iv, 681).—*o*-Naphthoylbenzoic acid is treated with hydrogen in the presence of contact metals or their oxides; platinum, palladium, nickel, and, in particular, nickel monoxide and sesquioxide are cited. Perhydrophenylnaphthylmethanecarboxylic acid, $C_{18}H_{30}O_2$, is thus obtained as a syrup containing crystals, from which four isomerides can be isolated; *α-acid*, rhombic platelets, m. p. 129°; *β-acid*, rhombic platelets, m. p. 114°; *γ-acid*, prisms, m. p. 94°; *δ-acid*, viscous liquid. Cautious concentration of a solution of the mixed acids in glacial acetic acid causes the separation of a mixture of α- and β-acids, and later of a mixture of the β- and γ-forms. Complete evaporation of the solvent leaves a viscous liquid consisting of the readily soluble and difficultly crystallisable δ-acid. The α- and β-acids can be separated by means of light petroleum, the β- and γ-isomerides by the same solvent or by ethyl acetate. The number of parts of light petroleum and ethyl acetate required for the solution of 1 gram of the various acids at 20° is for the α-acid (40, 23), β-acid (9, 10), and γ-acid (3·1, 3·6). The perhydrated acids are technically valuable as substitutes for the higher fatty acids. A perhydrated acid is not obtained when naphthoylbenzoic acid is boiled with coppered zinc dust and concentrated ammonia, phenylnaphthylmethane-*o*-carboxylic acid being produced. H. W.

Preparation of 3 : 5-Di-iodosalicylic Acid and its Solubility in Water. VICTOR COFMAN (*Gazzetta*, 1920, **50**, ii, 296—299).—The methods previously given for preparing 3:5-di-iodosalicylic acid yield a mixture of the latter with iodosalicylic acid, various iodophenols, and sometimes Lautemann's "red compound" (*Annalen*, 1861, **120**, 299). The di-iodo-acid may be obtained pure by the interaction of salicylic acid and iodine chloride in dilute acetic acid, and forms crystals beginning to darken at about 220°, m. p. 228—230° (decomp.); the temperature of decomposition was given by Lautemann (*loc. cit.*) as 212°, by Liechti (*Annalen*, 1870, Suppl. 7, 141) as 193—197°, and by Demole (*Ber.*, 1874, **7**, 1439) as 220—230°. Contrary to the view formerly held, that the iodination is due to a direct action of the iodine chloride, and to Richard's view (A., 1902, i, 280) that the true iodinating agent is iodic acid, the results of the author's experiments indicate that the action is due to hypoiodous acid: $ICl + H_2O = HOI + HCl$ and

$$2HOI + CO_2H{\cdot}C_6H_4{\cdot}OH = CO_2H{\cdot}C_6H_2I_2{\cdot}OH + 2H_2O$$

(T., 1919, **115**, 1040). The solubility of 3:5-di-iodosalicylic acid in water is 1 in 6000 at 10° and 1 in 5200 at 25°. T. H. P.

Action of Ammonia on Phenylpyruvic Acid and Benzylpyruvic Acid. J. BOUGAULT (*Bull. Soc. chim.*, 1921, [iv], **29**, 47—53).—When phenylacetylphenylalanine (compare Erlenmeyer and Kunlin, A., 1899, i, 761) is oxidised with potassium

permanganate in alkaline solution, *phenylglyoxylphenylalanine*, $CH_2Ph\cdot CH(CO_2H)\cdot NH\cdot CO\cdot COPh$, m. p. 118°, is obtained, giving a *semicarbazone*, m. p. 212° (decomp.). On hydrolysis it yields phenylalanine and phenylglyoxylic acid.

Benzylpyruvic acid when heated in a sealed tube with ammonia yields *phenylpropionylbenzylalanine amide*,

$$CH_2Ph\cdot CH_2\cdot CH(CO\cdot NH_2)\cdot NH\cdot CO\cdot CH_2\cdot CH_2Ph,$$

m. p. 185°, which when hydrolysed with dilute alkalis gives *phenylpropionylbenzylalanine*, m. p. 160°. W. G.

Bile Acids. VIII. Lithocholic Acid. HEINRICH WIELAND and PAUL WEYLAND (*Zeitsch. physiol. Chem.*, 1920, **110**, 123—142).—Lithocholic acid, $C_{24}H_{40}O_3$, is a normal constituent of bile, from which it is separated together with deoxycholic acid by precipitation as barium salts. The two acids are best separated by means of ether in which lithocholic acid is the more soluble. It crystallises from alcohol in hexagonal leaflets, m. p. 186°, and has $[\alpha]_D^{19}$ +23·33°. *Dehydrolithocholic acid*, $C_{24}H_{38}O_3$, obtained by treating a glacial acetic acid solution of lithocholic acid with chromic acid, evaporating, and extracting with ether, forms interwoven needles, m. p. 140—141°. *Cholenic acid*, $C_{24}H_{38}O_2$, nodules of thin needles, m. p. 153—154°, is formed on distilling lithocholic acid in a vacuum. Cholanic acid, $C_{24}H_{40}O_2$, obtained by reducing cholenic acid with hydrogen in the presence of palladium-black, crystallises from acetic acid in voluminous needles, m. p. 162—163°. By the action of nitric acid (D 1·4) on lithocholic acid, *lithobilianic acid*, $C_{24}H_{38}O_6$, is obtained as prisms, m. p. 279°. *Pyrolithobilianic acid*, $C_{23}H_{36}O_3$, m. p. 200—201°, is obtained by submitting lithobilianic acid to a temperature of 280—300° in a metal-bath in a current of nitrogen free from water and carbon dioxide. An isomeric *tricarboxylic acid*, $C_{24}H_{38}O_6$, m. p. 261°, was obtained by the action of nitric acid (D 1·4) on ketocholanic acid. A *pyro*-acid was prepared from the tricarboxylic acid by heating it in a vacuum at 280—300°, and then distilling at a temperature of 320°. It crystallises in lancet-shaped leaflets, m. p. 173—174°. S. S. Z.

Bile Acids. IX. The Mechanism of the Dehydration of the Bile Acids. HEINRICH WIELAND and ERICH BOERSCH (*Zeitsch. physiol. Chem.*, 1920, **110**, 143—152).—On heating cholic acid for two hours on a metal-bath at 200—210° water is driven off in the proportion of one molecule of water to two molecules of cholic acid. The residue consists of a mixture of 5% of cholic anhydride (dyslysin) with 95% of acid anhydrides. The cholic anhydride, $C_{48}H_{78}O_9$, is obtained from the residue by extracting it with alcohol as small crystals, m. p. 320—323°. On distilling the anhydride, cholatrienic acid is obtained. Deoxycholic acid treated in the above way lost water in the proportion of one molecule of water to two molecules of deoxycholic acid after two hours; on further heating, more water is lost. The deoxycholic anhydride, $C_{48}H_{78}O_7$, obtained from the residue, has m. p. 275—280°. Chola-

dienic acid is obtained on distilling the anhydride. By the action of concentrated hydrochloric acid on sodium cholate a mixture of various acids is obtained. *Triacetylcholic acid*, $C_{30}H_{46}O_8$, is obtained by saturating a solution of cholic acid in glacial acetic acid with hydrogen chloride; it has m. p. 257°. *Diformyl deoxycholic acid*, $C_{26}H_{40}O_6$, obtained by heating deoxycholic acid with 95% formic acid on the water-bath, crystallises in colourless prisms, m. p. 193°. On boiling deoxycholic acid with glacial acetic acid the *monoacetyl* derivative, $C_{26}H_{42}O_5$, is obtained, crystallising in colourless rhombohedral crystals, m. p. 115°. When crystallised from alcohol, the substance melted at 95° and then solidified and melted again at 161—162°. S. S. Z.

The Bile Acids. VII. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1920, **110**, 167—171).—Biloidanic acid, $C_{19}H_{28}O_{10}$, is prepared by oxidising bilianic acid with concentrated nitric acid (D 1·4). It crystallises in characteristic triangular crystals, decompose at 226—228°, and has $[\alpha]_D +14°$ (approx.) in alcohol.
S. S. Z.

The Bile Acids. VIII. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1920, **112**, 38—44).—The acid obtained by Letsch (A., 1909, i, 697) by the action of a mixture of nitric and sulphuric acids on cholic acid is identical with biloidanic acid. The neutral methyl ethers of both acids have also been found to be identical.
S. S. Z.

Natural and Synthetic Truxillic and Truxinic Acids. III. R. STOERMER and E. LAAGE (*Ber.*, 1921, **54**, [*B*], 77—85).—The known truxillic acids have been considered previously to be derived from the two series, $\begin{array}{l}\mathrm{Ph{\cdot}CH{\cdot}CH{\cdot}CO_2H}\\ \mathrm{CO_2H{\cdot}CH{\cdot}CH{\cdot}Ph}\end{array}$ and $\begin{array}{l}\mathrm{Ph{\cdot}CH{\cdot}CH{\cdot}CO_2H}\\ \mathrm{Ph{\cdot}CH{\cdot}CH{\cdot}CO_2H}\end{array}$ although the experimental evidence is not absolutely conclusive. If this is the case, there should be in all eleven acids, of which five are constituted according to the first and six according to the second formula. Until recently, however, only six of the isomerides have been isolated, and the possibility has therefore been considered by Stobbe (A., 1919, i, 329; compare Stoermer and Foerster, A., 1919, i, 444) that these are all members of the second series. The discovery of a seventh form (see following abstract) renders this idea untenable. For the sake of simplicity, it is now proposed to distinguish between the two series, which have nothing in common but their formation by the polymerisation of *trans*- and *cis*-cinnamic acids, by retaining the term truxillic for the former and denoting the latter as truxinic acids (*iso*truxillic acids of Stoermer and Foerster, *loc. cit.*); it is further proposed to replace the Greek letters in the latter series by a prefix derived from them, thus, for example, β-truxinic acid is termed betruxinic acid.

The action of light on 443 grams of *trans*-cinnamic acid led to

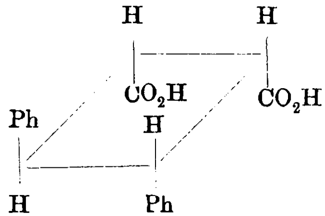
the formation of about 288 grams of α-truxillic acid, 4·3 grams of β-truxinic acid, and 0·5 gram of ε-truxillic acid (Hesse's β-cocaic acid), the remainder consisting of unchanged cinnamic acid, resinous products, and benzaldehyde. The formation of β-truxinic acid, which has otherwise only been prepared by illumination of *cis*-cinnamic acid, is ascribed to the partial transformation of the *trans*- into the *allo*-cinnamic acid, which then undergoes polymerisation. The method of examination consists in extracting the illuminated mixture of acids with alcohol and ether, which leaves the α-acid almost completely undissolved; the residue obtained after removal of the solvents is esterified with methyl alcohol and methyl cinnamate removed in a current of steam. The residual truxillic and truxinic esters are freed from resinous matter by distillation in a high vacuum, hydrolysed with alcoholic potassium hydroxide solution, and the sparingly soluble potassium β-truxinate is separated from the readily soluble potassium ε-truxillate. It appears that, in general, the truxinic acids yield nicely crystalline potassium salts which are very sparingly soluble in alcohol, whilst the potassium truxillates dissolve readily in this medium. *Ammonium β-truxinate*, needles, decomp. 187°, likewise dissolves very sparingly in cold alcohol.

The composition of the natural mixture of truxillic acids, in which Liebermann has previously proved the presence of the α- and β-acids, has been more fully investigated, the method used being practically identical with that applied to the product of the polymerisation of *trans*-cinnamic acid (see above). The relative proportions of the acids isolated varied somewhat in different experiments, but, under the most favourable conditions, were α-truxillic acid (25%), ε-truxillic acid (4·25%), β-truxinic acid (29%), δ-truxinic acid (10%), and *neotruxinic acid* (0·12%), the remainder consisting of benzoic and cinnamic acids with large quantities of resinous acids. The occurrence of γ-truxillic or ζ-truxinic acids could not be established, and the absence or presence in merely minimal amount of these acids, as also the small quantity of ε-truxillic and neotruxinic acids, is attributed to the fact that their formation involves the simultaneous polymerisation of a molecule of *cis*- and a molecule of *trans*-cinnamic acid, whereas α-truxillic acid is derived exclusively from *trans*- and β- and δ-truxinic acids exclusively from *cis*-cinnamic acid.

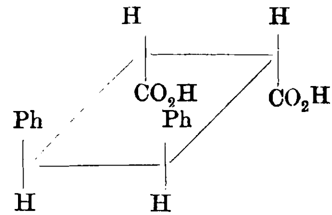
One hundred grams of glacial acetic acid dissolve 0·3174 gram of α-truxillic acid, 4·310 grams of δ-truxillic acid, and 22·96 grams of ε-truxillic acid at 20°. H. W.

The Sixth Acid of the Truxillic Acid Series, ζ-Truxinic Acid (Zetruxinic Acid). IV. R. Stoermer and F. Scholtz (*Ber.*, 1921, **54**, [*B*], 85—96).—ζ-Truxinic acid, the formation of which from δ-truxinic acid has been shortly indicated previously (Stoermer and Foerster, A., 1919, i, 445), is shown to be a *cis*-truxinic acid, which can be resolved into its optical antipodes and which must therefore have the formula (I). This result, considered

in conjunction with the possible formulæ for the various truxinic acid, indicates that β-truxinic acid is probably constituted in accordance with II.



(I.)



(II.)

β-Truxinic acid is converted into the δ-acid, m. p. 175°, either by fusion with eight times its weight of potassium hydroxide or by being heated with concentrated hydrochloric acid during six hours at 160°, and the latter is transformed into zetruxinic acid by treatment with acetic anhydride and sodium acetate for twenty-four hours on the water-bath or for three hours at 210°, or, preferably, by being heated with acetic anhydride alone at 160°. It crystallises in small needles, m. p. 239° (100 grams of glacial acetic acid dissolve 1·134 grams of β-, 10·382 grams of δ-, and 1·164 grams of ζ-truxinic acid at 20°; the corresponding figures for the β- and ζ-acids in 50% acetone are 2·469 and 2·343 grams). The ζ-acid is somewhat less readily esterified than the β- or δ-acid. It is reconverted into the latter by the action of concentrated hydrochloric acid at 140° or by fusion with potassium hydroxide. The *calcium* and *barium* salts of ζ-truxinic acid are almost insoluble in cold water, whilst the *potassium*, long, transparent needles, and *ammonium* salts, needles, decomp. ca. 160°, are almost insoluble in cold alcohol. The following derivatives of ζ-truxinic acid are described: *methyl* ester, colourless crystals, m. p. 116°; *methyl hydrogen* ester, m. p. 168°; *ethyl* ester, small, matted needles, m. p. 80°; *ethyl hydrogen* ester, m. p. 190°; *anhydride*, shining crystals, m. p. 150°, which is slowly reconverted by boiling water into the ζ-acid; *anil*, slender, colourless needles, m. p. 180°; *anilic acid*, m. p. 209°; *chloride*, prisms, m. p. 150°; *dianilide* (from the chloride and aniline in boiling benzene), m. p. 285°. Ammonium ζ-truxinate decomposes completely into ammonia and ζ-truxinic acid when heated in the usual manner at 210°, but, if compressed and then plunged in a bath at 170° which is raised to 200—210°, yields *ζ-truxinimide*, slender, shining needles, m. p. 168—168·5° (the *sodium* salt is described); the imide is moderately stable towards alkali, but is gradually transformed by alcoholic potassium hydroxide at the ordinary temperature into the *amide-acid*, slender, woolly needles, m. p. 222° (decomp.), which yields a sparingly soluble *sodium* salt.

ζ-Truxinic acid can be resolved into its optical antipodes with unusual readiness by means of cinchonine in 76% alcoholic solution, the alkaloidal salt of the *l*-acid being the more sparingly

soluble. *l*-ζ-*Truxinic acid* has m. p. 222°, $[\alpha]_D^{20}$ −78·37° in alcohol (96%), whilst the corresponding figures for the d-*acid* are 222° and +65·42°. The active acids are about four times as soluble as the racemic form. The *l*-acid is not racemised by treatment with boiling dilute sodium hydroxide solution or concentrated hydrochloric acid; when fused with potassium hydroxide it is smoothly converted into *r*-δ-truxinic acid. l-*Zetruxinic anhydride* has m. p. 162°, $[\alpha]_D^{20}$ −145·84° in acetone solution, whilst the corresponding *chloride* has m. p. 160°, $[\alpha]_D^{20}$ −98·62° in benzene solution. *Methyl* d-*zetruxinate* has m. p. 106°, $[\alpha]_D^{20}$ +89·88° in acetone solution.

H. W.

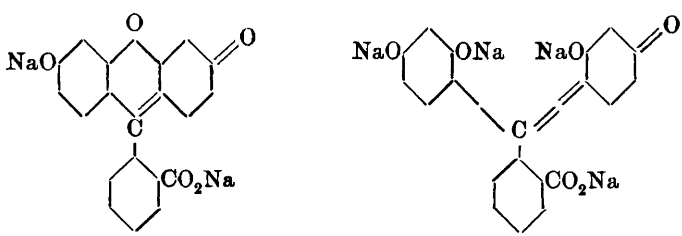
The Seventh Acid of the Truxillic Acid Series, Neotruxinic Acid. V. R. Stoermer and E. Laage (*Ber.*, 1921, **54**, [*B*], 96—101).—The presence of neotruxinic acid in the mixture of truxillic acids obtained during the preparation of cocaine has been demonstrated by Stoermer and Laage (this vol., i, 179), but the amount of it is very small and the isolation not invariably successful. Basing their experiments on the hypothesis of Stoermer and Foerster (A., 1919, i, 445), that the two meso- and eight optically active forms of the truxinic acids form a group which have properties analogous to those of the saccharic and mucic acids, the authors have studied the isomerisation of β-truxinic acid under the influence of pyridine, and have thus succeeded in preparing neotruxinic acid artificially. The latter is regarded provisionally as a *trans*-dicarboxylic acid, since it does not yield a corresponding imide, but the configuration cannot be definitely decided until attempts to prepare the anhydride and to resolve the acid are made.

β-Truxinic acid is heated for five hours at 160—170° with pyridine and water. Considerable difficulty is experienced in separating neo- from unchanged β-truxinic acid, which can only be partly effected by extraction with boiling 5% alcohol, as that leaves a part of the β-truxinic acid undissolved. The soluble acids are separated by conversion into their methyl esters, crystallisation of the latter from dilute methyl alcohol, and hydrolysis by cold alcoholic potassium hydroxide solution, or, preferably, by saturating the alcoholic solution of the acids with gaseous ammonia, and extraction of the precipitated ammonium salts with boiling 96% alcohol, which leaves the salt of the *neo*-acid undissolved. Isomerisation of β-truxinic acid can also be effected by dimethylaniline at 160—170°. Neotruxinic acid has m. p. 209—209·5°, and, in substance, exhibits a remarkable similarity to the β-acid. The crystalline *potassium* salt, which dissolves very sparingly in cold alcohol but readily in water, and the *calcium* salt are described. *Ammonium neotruxinate*, colourless, crystalline powder, m. p. 235° (decomp.), readily loses ammonia and yields neotruxinic acid when heated in the loosely-powdered state, but when firmly compressed and heated at 235—240° passes into β-*truxinimide*, m. p. 224—225°, which is also

obtained when *ammonium β-truxinate*, decomp. 187°, is heated at 200°. It is converted by hot sodium carbonate solution into the sparingly soluble *sodium* salt and by alcoholic potassium hydroxide into the *semi-amide* of β-truxinic acid, m. p. 193—194° (decomp.) [the *sodium* salt is described]. Neotruxinic acid is converted by phosphorus pentachloride in the presence of dry ether into the corresponding chloride, from which, by the action of aqueous ammonia, the *neotruxinamide*, small crystals, m. p. 249°, is smoothly prepared. β-Truxinyl chloride under similar conditions was only partly converted into *β-truxinamide*, matted needles, m. p. 239°, a mixture of resinous acids being produced simultaneously, from which the half amide of β-truxinic acid was isolated. *Methyl neotruxinate* crystallises in colourless needles, m. p. 126—127°, and, on hydrolysis, invariably gives small amounts of β- or δ-acid in addition to neotruxinic acid. Methyl β-truxinate has m. p. 76°. *Ethyl neotruxinate* could only be obtained as an oil, whereas the corresponding β-truxinic ester has m. p. 49—50°. H. W.

The Constitution of Thiofluorescein and its Technical Applications. TOSHIO MAKI (*J. Coll. Eng. Tokyo Imp. Univ.*, 1920, **11**, 1, 1—38).—The representation of thiofluorescein by Meyer and Szanecki (A., 1900, i, 660) as the sulphur analogue of fluorescein, $C_{20}H_{12}O_4S$, in which the chromophoric oxygen is replaced by sulphur, was incorrect, and was due to the analysis of an impure product.

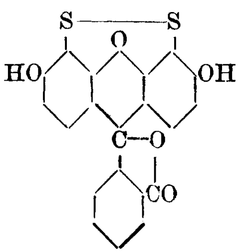
The author, who has studied the conditions of formation of thiofluorescein from fluorescein under a variety of conditions, finds that it is formed at temperatures between 110° and 150° slowly and incompletely by the action of sodium polysulphide, more readily by sodium sulphide, and with particular ease in the presence of free alkali hydroxide. Fluorescein (I) does not combine readily with sulphur below 200°, but when heated with alkali hydroxide at 100—140° the pyrone ring is opened, and the resulting compound (II) is sulphurised with ease:



(I.) (II.)

The presence of water is necessary as sulphuration does not occur at these temperatures in its absence. Under suitable conditions, a yield of 94% of the theoretical of thiofluorescein is obtained. The reaction is complete when a diluted sample shows no fluorescence. The product is dissolved in water, acidified, and the precipitate

collected. A neutral solution of the ammonium salt is left overnight, when the major portion of the free sulphur is precipitated. The product obtained when the filtrate is acidified is extracted with ether several times to remove sulphur and unchanged fluorescein, and converted into the normal sodium salt. The latter is precipitated from a concentrated aqueous solution, on the addition of much alcohol, as a crystalline powder. It is filtered, dissolved in water, acidified in presence of ferric chloride, boiled, filtered, the precipitate extracted with ether, crystallised from a mixture of acetone and alcohol, and dried at 120°. Thiofluorescein is a light brick-red powder of high m. p. and darkening without decomposition at 300°, insoluble or very sparingly soluble in most solvents, but readily soluble in acetone containing 10—15 per cent. water, without fluorescence. The sodium, potassium, and ammonium salts are crystalline powders with a fine, green or greenish-yellow metallic lustre, and dissolve readily in water, forming scarlet-red solutions, without fluorescence. Thiofluorescein has the composition $C_{20}H_8O_3S_2(OH)_2$, and its constitution as fluorescein disulphide (annexed formula) has been determined by a study of its behaviour on reduction, oxidation, bromination, and nitration, supported by examination of the absorption spectra. Thiofluorescein dissolves in alkaline reducing agents with a deep violet-blue colour, owing to the formation of the corresponding mercaptan, thiogallein; this colour changes to the scarlet-red of the alkali salts of thiofluorescein on oxidation in air. The oxidation of thiofluorescein with alkaline permanganate proceeds quantitatively, thus:



$$R{<}\begin{matrix}S\\ |\\ S\end{matrix} + 5O + H_2O = R{<}\begin{matrix}SO_3H\\ SO_3H\end{matrix}$$

Thiofluorescein.

$$R{<}\begin{matrix}SO_3H\\ SO_3H\end{matrix} + 2H_2O = R{<}\begin{matrix}H\\ H\end{matrix} + 2H_2SO_4$$

Fluorescein.

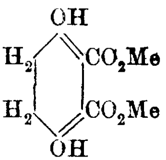
owing to the instability of fluorescein sulphonic acid, and the ease with which it is hydrolysed.

When treated with bromine in cold ethyl alcoholic solution, thiofluorescein is not brominated, but some oxidation occurs, whilst when the mixture is boiled, thiofluorescein is converted completely into a mixture of eosin (tetrabromo-fluorescein) and ethyleosin. This result is explained by the preliminary oxidation of the thiofluorescein to fluorescein, sulphuric and hydrobromic acids, followed by the bromination of the fluorescein to eosin, some of which is ethylated by the ethyl bromide formed during the reaction. The nitration of thiofluorescein in sulphuric acid solution with $2\frac{1}{2}$ mols.

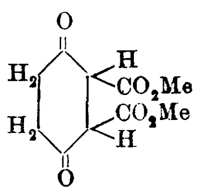
of nitric acid (D 1·5) yields a dinitro-derivative, $C_{20}H_8O_9N_2S_2$, oxidised by alkaline permanganate to dinitrofluorescein, which yields 4-nitroresorcinol, m. p. 113°, when heated with concentrated sodium hydroxide at 140°. Thiofluorescein is an acid dye producing orange-brown shades faster than those obtained with fluorescein, whilst thiogallein is a powerful mordant dye which produces shades closely related to those of gallein, although deeper and faster than the latter. [See, also, *J. Soc. Chem. Ind.*, 1921, 143A.]

F. M. R.

Synthesis of Methyl *cyclo*Hexane-1 : 4-dione-2 : 3-dicarboxylate, an Orthoisomeride of Succinylsuccinic Ester. BURCKHARDT HELFERICH (*Ber.*, 1921, **54**, [*B*], 155—162).—3 : 6-Dihydroxy-*o*-phthalic acid (Thiele and Günther, A., 1906, i, 743) is converted by methyl alcohol and sulphuric acid into *methyl* 3 : 6-*dihydroxy*-o-*phthalate*, colourless needles, m. p. 141—142° (corr.) after slight softening (the *sodium* salt, yellow, amorphous powder, which decomposes on exposure to air, and the *dimethyl ether*, short prisms, m. p. 102—103° (corr.), are described). The similarly prepared *ethyl* ester has m. p. 89°. The methyl ester is reduced by sodium amalgam in cold alkaline solution to *methyl* cyclo*hexane*-1 : 4-*dione*-2 : 3-*dicarboxylate* (annexed formula I or II), short prisms, m. p. 55—57° (corr.), the constitution of which is deduced from the observations that its aqueous or alcoholic solution gives a dark red coloration with ferric chloride, that it is soluble in alkalis and precipitated from such solutions by carbon dioxide, that a *disodium* salt, nearly colourless powder, which rapidly oxidises on exposure to air, can be obtained from concentrated alcoholic solution, that it gives a *disemicarbazone*, needles, m. p. 177—178° (corr.), and that it is hydrolysed by boiling dilute sulphuric acid to *cyclo*hexane-1 : 4-dione.

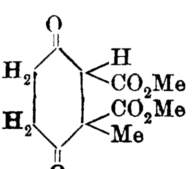


(I.)



(II.)

Methyl 3-*methyl*cyclo*hexane* - 1 : 4 - *dione*-2 : 3-*dicarboxylate* (annexed formula), m. p. 92° (corr.) after softening at 89°, is smoothly prepared by the action of methyl iodide and sodium methoxide on an ice-cold solution of methyl *cyclo*hexane-1 : 4-dione-2 : 3-dicarboxylate in methyl alcohol. The new ester is soluble in alkali, yields a red coloration with ferric chloride, and gives a *diphenylhydrazone*; it is hydrolysed by boiling dilute sulphuric acid to 3-*methyl*cyclo*hexane*-1 : 4-*dione*, silvery leaflets, m. p. 50°, which does not give a coloration with ferric chloride [*semicarbazone*, m. p. about 240° (decomp.)].



Whilst methyl *cyclo*hexane-1 : 4-dione-2 : 3-dicarboxylate is un-

affected or only very slowly reduced by sodium amalgam in alcoholic solution at 0°, the corresponding 3-methyl derivative is readily hydrogenated; the product has not been obtained in the crystalline form up to the present, but, when boiled with dilute sulphuric acid, it gives a small amount of an *acid*, m. p. 154° (corr.), after slight softening, which from its mode of formation is regarded as 3-methyl*cyclo*hexane-1-one-4-ol-3-carboxylic acid. H. W.

Derivatives of Gallic Acid. II. Gallic Acid (and the Cresotic Acids) and Chloral. RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM (T., 1921, **119**, 201—209).

Condensation of *p*-Nitrobenzyl Chloride with Nitroso-compounds. A New Mode of Formation of *N*-Oximino-ethers. FRED BARROW and EVAN DALTON GRIFFITHS (T., 1921, **119**, 212—216).

Dihydroxynaphthaldehydes. GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1921, **119**, 177—187).

Action of the Three Isomeric Ethylaminobenzoic Acids on Benzo- and Tolu-quinones. B. LINKE (*J. pr. Chem.*, 1920, [ii], **101**, 265—272).—The results obtained conform to those observed in previous cases (Ville and Astre, A., 1895, i, 465; Suchanek, A., 1915, i, 269; H. and W. Suida, A., 1919, i, 79). 2:5-*Bisethyl*-o-*carboxyanilino*-p-*benzoquinone*,

$$(CO_2H\cdot C_6H_4\cdot NEt)_2\cdot C_6H_2{<}^{O}_{O},$$

is a brown powder; the *meta*-derivative, $C_{24}H_{22}O_6N_2$, a dark brown, crystalline powder; the *para*-derivative, $C_{24}H_{22}O_6N_2$, dark red crystals. 2-*Ethyl*-o-*carboxyanilino*-p-*benzoquinone*,

$$(CO_2H\cdot C_6H_4\cdot NEt)\cdot C_6H_3{<}^{O}_{O},$$

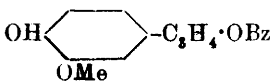
a dark brown, crystalline powder; the *meta*-derivative, $C_{15}H_{13}O_4N$, a dark brown, crystalline powder; the *para*-derivative, $C_{15}H_{13}O_4N$, a black, crystalline substance. The corresponding *monoanilides*, $C_{16}H_{15}O_4N$, from toluquinone, are respectively dark violet, dark violet, and reddish-brown. J. K.

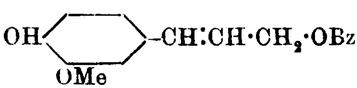
Electrolytic Reduction of Menthone. MOTOOKI MATSUI and SHIU SHIMIZU (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 245—264).—Menthone can only be reduced electrolytically in acid solution (sulphuric or hydrochloric). The best results were obtained using an amalgamated tin or lead cathode, the cathode solution consisting of a mixture of 75% sulphuric acid (40—45 c.c.) with 94% alcohol (35—40 c.c.) at a temperature below 15°. The current used was 6—8 amperes/100 sq. cm. at 11—13 volts. The yield of menthol obtained was at the best 25% of the theoretical, and the product was purified with difficulty. An oily by-product, which

was always formed, may be menthane. The quantity of this substance was increased by using a more dilute acid for the cathode solution. E. H. R.

Constituents of Resins. VII. Lubanyl Benzoate from Siamese Benzoin. I. ALOIS ZINKE and JOHANNA DZRIMAL (*Monatsh.*, 1920, **41**, 423—441. Compare this vol., i, 39).—Lubanyl benzoate, obtained by Reinitzer (A., 1915, i, 431), and regarded by him as the benzoate corresponding with an unknown resin alcohol, lubanol, appears to be similar to guaiacresinol (Schroeter, Lichtenstadt, and Irineu, A., 1919, i, 84) and to lariciresinol and pinoresinol (Bamberger and collaborators). Its molecule contains a benzoyloxy-group, a methoxyl group, a free phenolic hydroxyl group, and a double linking. Analysis of the benzoate and its derivatives leads to the formula $C_{17}H_{16}O_4$, and this, minus OBz, OMe, and OH, gives C_9H_7, which presumably contains a benzene nucleus, and must contain the double linking.

Lubanyl benzoate readily undergoes change in the air, giving an odour of vanillin, this being observed also when the benzoate and certain of its derivatives are oxidised in other ways. Further, when lubanyl benzoate is submitted to dry distillation, the products formed include benzoic acid, eugenol, or *iso*eugenol, and, apparently, guaiacol (compare Bamberger and Vischner, A., 1900, i, 605; 1901, i, 220). These results indicate for lubanyl benzoate the annexed structure; since eugenol is formed on reduction, the C_3H_4 residue must represent a direct chain and must contain the double linking, and it is possible that lubanyl benzoate is the benzoate corresponding with coniferyl alcohol, its structure then being as annexed.





Hydrolysis of lubanyl benzoate yields almost white or brownish-red, amorphous products, and the composition of some of these corresponds with that of coniferyl alcohol. According to Tiemann and Haarmann (this Journ., 1874, 895; 1876, i, 76), alkaline solutions of coniferyl alcohol, even when cautiously acidified, always yield only an amorphous polymerisation product, which is shown by further investigation to be probably identical with the product of hydrolysis of lubanyl benzoate.

Compounds like guaiacresinol and lubanyl benzoate, although not related chemically to cholesterol, yet give cholesterol reactions. H. Wiesler has now tried these reactions on a number of simpler compounds, the results indicating that such reactions are useless for the characterisation of groups.

Lubanyl benzoate, $C_{17}H_{16}O_4$, forms nodulous, drusy masses or occasional hexagonal plates, m. p. 72° (uncorr.), dissolves in concentrated sulphuric acid, giving a solution which is blood-red in thick and violet in thin layers, and in alcoholic solution gives an emerald-green coloration with ferric chloride. Its *dibromide*,

$C_{17}H_{16}O_4Br_2$, forms crystals, m. p. 119—120°, dissolves in concentrated sulphuric acid, giving a yellow solution turning to violet and then to blue when heated, and in alcoholic solution yields a pale green coloration with ferric chloride.

Lubanyl dibenzoate [*benzoyl-lubanyl benzoate*], $C_{24}H_{20}O_5$, forms white needles, sintering at 70°, m. p. 79—80°, gives no coloration with ferric chloride, and dissolves in concentrated sulphuric acid, yielding a solution blood-red in thick and violet in thin layers. Its *dibromide*, $C_{24}H_{20}O_5Br_2$, crystallises in bundles of broad needles sintering at 150°, m. p. 153—154°, and dissolves in cold concentrated sulphuric acid, giving a greeenish-yellow solution, which becomes green and then blue when heated.

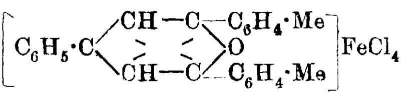
The substance, $C_{10}H_{12}O_3$ (?), obtained by hydrolysing lubanyl benzoate, melts indistinctly at 110—120°, dissolves in concentrated sulphuric acid to a violet solution, and in alcoholic solution gives a green coloration with ferric chloride. Addition of water to its hot acetic acid solution yields a precipitate, which, when boiled with water, forms a brown, crumbly mass darkening at 160°, beginning to sinter at 170° and to melt at 210°, and decomposing at 217°. Its composition agrees with the formula $C_{20}H_{22}O_5$ or $C_{20}H_{24}O_5$, so that it may be formed, by loss of either water or oxygen, from the substance, $C_{10}H_{12}O_3$. Further, in composition and properties it agrees with Lüdy's siaresinotannol (A., 1893, i, 666), for which the formula $C_{12}H_{14}O_3$ was suggested by this author.

The following crystallographic data have been obtained. *d*-Siaresinol acetic acid (Zinke and Lieb, A., 1918, i, 398) forms thin, hexagonal plates, possibly of the rhombic system. The acid, $C_{27}H_{40}O_4$, from siaresinolic acid (Zinke and Lieb, A., 1919, i, 128), forms crystals of the rhombic system, $a:b:c=0{\cdot}444:1:1{\cdot}273$. The acid, $C_{27}H_{40}O_3$, from *d*-sumaresinolic acid (Zinke, A., 1920, i, 65) forms twinned crystals, $a:b:c=0{\cdot}728:1:1{\cdot}918$, $\alpha=89°11'$, $\beta=120°9\frac{1}{2}'$, $\gamma=91°30°$. T. H. P.

The Constitution of Catechin. III. Synthesis of Acacatechin. MAXIMILIAN NIERENSTEIN (T., 1921, **119**, 164—170).

Pyrylium Compounds. VIII. W. DILTHEY [with G. BAURIEDEL, G. GEISSELBRECHT, A. SEEGER, and J. WINKLER] (*J. pr. Chem.*, 1920, [ii], **101**, 177—206. Compare A., 1920, i, 323, 324).—It has previously been shown that the colourless ψ-bases (pyranols) corresponding with the arylpyrylium salts have the formula OH·CR:CH·CR:CH·COR. Applying this to the benzopyranols, two formulæ are possible: $O:C_6H_4:CH\cdot CH:CR\cdot OH$ and $OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot R$. Of these, the former is excluded, as representing a coloured compound, whilst the latter is an *o*-hydroxychalkone. These compounds are, however, not the true ψ-bases in question, since they only give pyrylium salts with concentrated acids, and are not regenerated from these (Decker and Fellenberg, A., 1907, i, 950; 1909, i, 116). Details are now promised, however, of the conversion of a *p*-methoxybenzopyrylium salt into the

corresponding hydroxychalkone, and in consequence it is suggested that benzopyranols and *o*-hydroxychalkones are stereoisomeric syn- and anti-forms respectively. Probably, also, the colour of bluish-violet alkali salts of xanthone dyes is due to their constitution as salts of the unsaturated enolic 1:5-diketones represented above (compare Baeyer, A., 1910, i, 249). The product of reducing α-hydroxy-ϵ-keto-$\alpha\gamma\epsilon$-triphenyl-$\Delta^{\alpha\gamma}$-pentadiene in presence of palladium has the formula $C_{23}H_{18}O$, and is probably 2:4:6-*triphenylpyran*; it undergoes gradual oxidation in sulphuric acid solution to the corresponding pyryl salt. $\alpha\epsilon$-Diketo-γ-phenyl-$\alpha\epsilon$-di-*p*-tolylpentane (Kostanecki, A., 1896, i, 688) is best prepared by the condensation of *p*-tolyl methyl ketone with its benzylidene derivative. Its colourless solution in sulphuric acid gradually becomes yellow with a green fluorescence, probably owing to formation of pyrylium salts. The *disemicarbazone*, $C_{27}H_{30}O_2N_6$, has m. p. 237—238°. 4-*Phenyl*-2:6-*di*-p-*tolylpyryl ferrichloride* (annexed formula), brownish-yellow crystals, m. p. 258°, on treatment with sodium carbonate, gives the ψ-base, α-*hydroxy*-ϵ-*keto*-γ-*phenyl*-$\alpha\epsilon$-*di*-p-*tolyl*-$\Delta^{\alpha\gamma}$-*pentadiene*, $C_6H_4Me{\cdot}C(OH){:}CH{\cdot}CPh{:}CH{\cdot}CO{\cdot}C_6H_4Me$, m. p. 101° (*disemicarbazone*, $C_{27}H_{28}O_2N_6$, m. p. 214—215°; *picrate*, $C_{31}H_{23}O_8N_3$, yellowish-red prisms, m. p. 260° [decomp.]; *perchlorate*, $C_{25}H_{21}O_5Cl$, golden-yellow prisms, m. p. 274—275°).



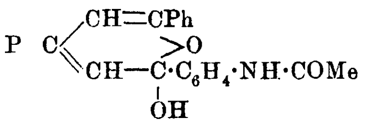
2:4-*Diphenyl*-6-p-*tolylpyryl ferrichloride*, $C_{24}H_{19}OCl_4Fe$, has m. p. 260°. α-*Hydroxy*-ϵ-*keto*-$\alpha\gamma$-*diphenyl*-ϵ-p-*tolyl*-$\Delta^{\alpha\gamma}$-*pentadiene*, $C_{24}H_{20}O_2$, yellow needles, m. p. 105° (*picrate*, $C_{30}H_{21}O_8N_3$, orange crystals, m. p. 245—246°; *zincichloride*, $C_{24}H_{19}OCl_3Zn$, orange crystals, m. p. 253° [decomp.]), has the constitution

$$OH{\cdot}CPh{:}CH{\cdot}CPh{:}CH{\cdot}CO{\cdot}C_6H_4Me$$

rather than $C_6H_4Me{\cdot}C(OH){:}CH{\cdot}CPh{:}CH{\cdot}COPh$, since with alcoholic sodium hydroxide it gives *p*-methylbenzoylformic acid and benzoic acid. Acetyldiphenyl (Willgerodt, A., 1910, i, 392; Vörlander, A., 1908, ii, 22; Adam, A., 1888, 959) is a *p*-derivative, since it gives diphenyl-4-carboxylic acid on oxidation; *benzylidene* derivative, $C_{21}H_{16}O$, yellow leaflets, m. p. 156°; *anisylidene* derivative, $C_{22}H_{18}O_2$, yellow prisms, m. p. 140°; *cinnamylidene* derivative, $C_{23}H_{18}O$, yellow needles, m. p. 160°. 4:6-*Diphenyl*-2-*diphenylylpyryl ferrichloride*, $C_{29}H_{21}OFeCl_4$, brownish-red crystals, m. p. 248°, is obtained from acetyldiphenyl and phenyl styryl ketone in presence of acetic anhydride and ferric chloride; the *picrate*, $C_{35}H_{23}O_8N_3$, red needles, m. p. 222°; *perchlorate*, $C_{29}H_{21}O_5Cl$, yellow needles, m. p. 236°; *perbromide*, $C_{29}H_{21}OBr_3$, red needles, m. p. 228—230°; ψ-*base*, $C_{29}H_{22}O_2$, needles, m. p. 133° (*disemicarbazone*, $C_{31}H_{28}O_2N_6$, needles, m. p. 218°). p-*Chlorophenyl styryl ketone*, $CHPh{:}CH{\cdot}CO{\cdot}C_6H_4Cl$, m. p. 101°. 4-*Phenyl*-2:6-*di*-p-*chlorophenylpyryl ferrichloride*, $C_{23}H_{15}OCl_6Fe$, yellowish-red needles, m. p. 292°. α-*Hydroxy*-ϵ-*keto*-γ-*phenyl*-$\alpha\epsilon$-*di*-p-*chlorophenyl*-$\Delta^{\alpha\gamma}$-*pentadiene*,

$$C_6H_4Cl{\cdot}C(OH){:}CH{\cdot}CPh{:}CH{\cdot}CO{\cdot}C_6H_4Cl,$$

needles, m. p. 118° (*zincichloride*, $C_{23}H_{15}OCl_5Zn$, yellowish-brown, m. p. 295°). *γδε-Triphenyl-α-*p*-chlorophenyl-αε-diketopentane*, $C_6H_4Cl·CO·CH_2·CHPh·CHPh·COPh$, prisms, m. p. 231°, from deoxybenzoin and *p*-chlorophenyl styryl ketone, does not react with ferric chloride. p-*Bromophenyl styryl ketone*, $C_{15}H_{11}OBr$, prisms, has m. p. 104—105° (compare Kohler, Heritage, and Burnley, A., 1910, i, 562). 2:4-*Diphenyl*-6-p-*bromophenylpyryl ferrichloride*, $C_{23}H_{16}OFeCl_4Br$, brownish-yellow, m. p. 279—280° (*ψ-base*, $C_{23}H_{17}O_2Br$, m. p. 103—104°), is obtained either from *p*-bromophenyl styryl ketone and acetophenone, or from phenyl styryl ketone and *p*-bromoacetophenone, as would be expected from the formula previously advocated for these salts (A., 1920, i, 324). 4 : 6 - *Diphenyl-2-α-naphthylpyryl ferrichloride*, $C_{27}H_{19}OCl_4Fe$, brownish-red, has m. p. 184°. 4:6-*Diphenyl-2-β-naphthylpyryl ferrichloride*, $C_{27}H_{19}OCl_4Fe$, m. p. 264°, is formed much more readily than the α-derivative from phenyl styryl ketone and the corresponding naphthyl methyl ketone. Acetyl - 4 - violonimine (annexed formula), prisms, m. p. 157—158°, from phenyl styryl ketone and acetyl-*p*-aminoacetophenone (*picrate*, $C_{31}H_{22}O_9N_4$, yellowish-red needles, m. p. 242°; *picrolonate*, $C_{35}H_{27}O_7N_5$, yellowish-red prisms, m. p. 233—234° [decomp.]), on hydrolysis furnishes violonimine, characterised by its *picrate*, $C_{29}H_{20}O_8N_4$, m. p. 273° (decomp.).



J. K.

Pyrylium Compounds. IX. Pyrylium Salts with meta-Substituents. W. Dilthey and Chr. Bloss (*J. pr. Chem.*, 1920, [ii], **101**, 207—212).—Pyrylium salts containing a para-hydroxyl group furnish, in place of the colourless *ψ*-bases, coloured anhydrobases (clarones) (A., 1920, i, 324). As would be anticipated, the corresponding meta-derivatives yield the normal *ψ*-bases, but a violet intermediate product may be observed when dilute sodium hydrogen carbonate solution is carefully added to the chloride of the *ψ*-base described below, and is possibly due to an unstable product similar in character to triphenylmethyl.

2:4-*Diphenyl*-6-m-*methoxyphenylpyryl ferrichloride*, $C_{24}H_{19}O_2Cl_4Fe$, prisms, m. p. 205°. *α-Hydroxy-ε-keto-αγ-diphenyl-ε-*m*-methoxyphenyl-$\Delta^{\alpha\gamma}$-pentadiene*, $C_{24}H_{20}O_3$, yellow needles, m. p. 114—115° (*picrate*, $C_{30}H_{21}O_9N_3$, golden-yellow needles, m. p. 176°; *acid chloride*, $C_{24}H_{20}O_2Cl_2$, yellow needles, m. p. 180°; *disemicarbazone*, $C_{26}H_{26}O_3N_6$, prisms, m. p. 196—198°); on demethylation with hydrochloric acid it gives 2:4-*diphenyl*-6-m-*hydroxyphenylpyryl chloride*, $C_{23}H_{17}O_2Cl$, orange needles, m. p. 210—212°. *α-Hydroxy-ε-keto-αγ-diphenyl-ε-*m*-hydroxyphenyl - $\Delta^{\alpha\gamma}$ - pentadiene*, $C_{23}H_{18}O_3$, needles, decomp. 120° (*picrate*, $C_{29}H_{19}O_9N_3$, orange needles, m. p. 268°; *bromide*, $C_{23}H_{17}O_2Br$, yellowish-red needles, m. p. 271—272°; *perbromide*, $C_{23}H_{17}O_2Br_3$, orange needles, m. p. 184—185°; *iodide*, $C_{23}H_{17}O_2I$, orange needles, m. p. 256—257°;

periodide, $C_{23}H_{17}O_2I_3$, brownish-violet leaflets, m. p. 233°; *disemicarbazone*, $C_{25}H_{24}O_3N_6$, prisms, m. p. 209° [decomp.]), on treatment with potassium hydroxide gives benzoic acid, acetophenone, and *m*-hydroxyacetophenone. J. K.

Compounds of Thiophen. I. Isomeric *n*-Propyl- and *iso*Propyl-thiophens. HELMUT SCHEIBLER and MARTIN SCHMIDT (*Ber.*, 1921, **54**, [*B*], 139—154).—The probable occurrence of thiophen derivatives in shale tar oils has led the authors to investigate the 1- and 2-propyl- and *iso*propyl-thiophens with the object of obtaining well-defined derivatives which would provide a means for the ready identification of the parent substances; the *p*-nitrophenylhydrazones of the acetylated substances appear most suitable for this purpose.

Ethyl γ-bromo-αα-dimethylacetoacetate, b. p. 114—116°/12 mm., is condensed with ethyl sodiomalonate in the presence of anhydrous ether to form ethyl β-methyl-γ-keto-βεε-tricarboxylate,

$$CH(CO_2Et)_2{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et,$$

greenish-yellow, viscous oil, b. p. 188—189° (corr.)/12 mm., and the latter is hydrolysed initially by moderately dilute boiling sulphuric acid and ultimately by aqueous sodium hydroxide to δδ-dimethyl-lævulic acid, $CHMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, m. p. 41°, in agreement with the datum of Conrad (A., 1897, i, 323). The sodium salt of this acid when distilled with phosphorus trisulphide yields 2-*iso*propylthiophen, colourless liquid, b. p. 152—153° (corr.), D_{20}^{20} 0·9691, D_4^{20} 0·9674, n_D^{20} 1·5030, M_D^{20} 38·53, Σ_D^{20} 30·56, $n_F - n_C$ 0·01447. The action of acetyl chloride and aluminium chloride on *iso*propylthiophen in the presence of carbon disulphide gives an 84% yield of 5-*acetyl*-2-iso*propylthiophen*, colourless liquid, b. p. 129—131° (corr.)/22 mm., n_D^{20} 1·5428 (small amounts of more highly acetylated products appear to be also formed); the *oxime* forms colourless crystals, m. p. 74°, whilst the p-*nitrophenylhydrazone* crystallises in thin needles, m. p. 198° (corr.). 5-*Benzoyl*-2-iso*propylthiophen* is a pale yellow oil, b. p 209—210° (corr.)/18 mm.

2-Propionylthiophen, b. p. 225—229°, is reduced by amalgamated zinc (the use of zinc wool in place of the granulated metal is recommended) and hydrochloric acid to 2-*n*-propylthiophen, colourless liquid, b. p. 157—160° (corr.), D_0^{20} 0·9700, D_4^{20} 0·9683, n_D^{20} 1·5048, M_D^{20} 38·61, Σ_D^{20} 30·62, $n_F - n_C$ 0·01447. The latter is converted by acetyl chloride into 5-acetyl-2-*n*-propylthiophen, pale yellow liquid, b. p. 257—260° (corr.), n_D^{20} 1·5438, which gives an oxime, m. p. 55°, and a p-*nitrophenylhydrazone*, m. p. 206° (corr.).

3-*iso*Propylthiophen, b. p. 153—156° (corr.), D_{20}^{20} 0·9750, D_4^{20} 0·9733, n_D^{20} 1·5052, M_D^{20} 38·44, Σ_D^{20} 30·48, $n_F - n_C$ 0·01409, is prepared from *iso*propylsuccinic acid. The acetyl derivative boils indefinitely at 115—128° (corr.)/15 mm., and thus appears to be a mixture of isomerides; the *oxime* is oily, but the p-*nitrophenylhydrazone* forms brownish-yellow needles, m. p. 141° (corr.).

Ethyl *n*-propylsodiomalonate is condensed with ethyl chloroacetate in boiling alcoholic solution to ethyl pentane-αββ-tricarboxyl-

ate, colourless liquid, b. p. 184° (corr.)/18 mm., which is converted into *n*-propylsuccinic acid by hydrolysis and subsequent elimination of carbon dioxide. Distillation with phosphorus sulphide converts the sodium salt of the acid into 3-n-*propylthiophen*, colourless liquid, b. p. 160—162° (corr.), D^{20} 0·9733, D_4^{20} 0·9716, n_D^{20} 1·5057, M_D^{20} 38·54, Σ_D^{20} 30·56, $n_F - n_C$ 0·01438. The corresponding acetylated *derivative*, b. p. 121—132°/22 mm., n_D^{20} 1·5426, appears to be a mixture of isomerides, which, however, cannot be separated by fractionation; the crude *oxime* obtained from it melts indefinitely at 46—59°, but after repeated crystallisation yields a fraction of sharp melting point, 108°. The p-*nitrophenylhydrazone* forms brownish-red needles, m. p. 171° (corr.).

The 2-substituted thiophens give a reddish-brown coloration when warmed with isatin and concentrated sulphuric acid, whereas the 3-derivatives yield dark blue dyes. Further, if a trace of the substituted thiophen is added to an ice-cold solution of phenanthraquinone in glacial acetic acid, and concentrated sulphuric acid is cautiously added, an intensely cherry-red ring is formed at the junction of the two liquids in the case of the 2-derivatives, whilst with the 3-compounds an olive-green ring is obtained. H. W.

Extractive Substances of Muscular Tissue. XX. Carnosine and its Compounds. I. A. Smorodincev (*Russ. Physiol. J.*, 1919, **2**, 285—297).—Descriptions are given of carnosine and its methods of extraction, and also of the known derivatives of carnosine, the following being now described for the first time. The *sulphate*, $(C_9H_{14}O_3N_4)_2,H_2SO_4$, decomposes at 238—240°, the *orthophosphate* at 205—207°, the *metaphosphate* at 200—203°, the *iodate* at 188—190°, and the *oxalate*, $(C_9H_{14}O_3N_4)_2,C_2H_2O_4$, at 216—218°. The *phosphotungstate*,

$$(C_9H_{14}O_3N_4)_3,12WO_3,P_2O_5,16H_2O,$$

is very slightly soluble in water, turns blue in the light, and remains undecomposed at 250°. The *phenylcarbamido*-derivative, $C_9H_{14}O_3N_4,C_6H_5\cdot NCO(+1\frac{1}{2}H_2O$ or $\frac{1}{2}Et\cdot OH)$, decomposes at 178—180°. T. H. P.

A Simple Method of Preparation of Creatine from Meat Extract. H. Steudel (*Zeitsch. physiol. Chem.*, 1921, **112**, 53—54). —The creatine is extracted from Liebig's meat extract with absolute alcohol on a water-bath. It crystallises on removing the alcohol by distillation. One kilo. of extract yields 25—30 grams of air-dry creatine. S. S. Z.

The Muscarine Question. II. ψ-Muscarine (Synthetic Muscarine). Albert B. Weinhagen (*Zeitsch. physiol. Chem.*, 1920, **112**, 13—27).—On the assumption that synthetic muscarine is identical with the natural base, but that the difference in the pharmacological action is due to the presence of by-products, the author has studied the various products resulting, in addition to synthetic muscarine, from the action of nitric acid on choline

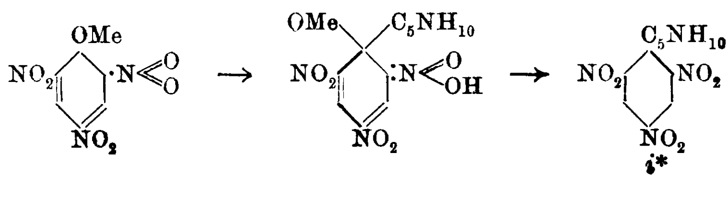
platinichloride. Besides the nitrous ester of the double salt, a compound similar to that described by Ewins, various other substances, including trimethylamine, were identified. It is assumed that such degradation products may be responsible for the curare-like action of "synthetic muscarine." S. S. Z.

Derivatives of 1 : 4-Diketones and Semicarbazide. E. E. Blaise (*Compt. rend.*, 1921, **172**, 221—223).—Under the ordinary conditions the 1 : 4-diketones give with semicarbazide simply disemicarbazones, which are, however, readily converted into 1-carbamidopyrroles. The disemicarbazone of acetonylacetone,

$NH_2 \cdot CO \cdot NH \cdot N:CMe \cdot CH_2 \cdot CH_2 \cdot CMe:N \cdot NH \cdot CO \cdot NH_2$,

when warmed on a water-bath with formic acid and then an excess of water added, yields 1-*carbamido*-2 : 5-*dimethylpyrrole*, m. p. 245°, which, when reduced with zinc and hydrochloric acid, gives 2 : 5-dimethylpyrroline. 1-*Formylamino*-2 : 5-*dimethylpyrrole*, m. p. 178°, obtained from formylhydrazine and acetonylacetone, is hydrolysed by aqueous potassium hydroxide, yielding 1-*amino*-2 : 5-*dimethylpyrrole*, m. p. 52°, b. p. 109°/21 mm., which with *iso*cyanic acid gives the 1-carbamido-2 : 5-dimethylpyrrole described above. 1-*Acetylamino*-2 : 5-*dimethylpyrrole*, m. p. 138—139°, undergoes a complex decomposition on hydrolysis. W. G.

Additive Compounds and the Process of Substitution in the Benzene Ring. V. Organic Molecular Compounds. M. Giua, A. Marcellino, and A. Curti (*Gazzetta*, 1920, **50**, ii, 300—312).—*s*-Trinitroanisole and piperidine, either directly or in alcoholic solution, yield a moderately stable additive compound, whilst in alcoholic solution containing sodium carbonate these two compounds react, yielding picrylpiperidine (compare Turpin, T., 1891, **59**, 716; Schotten and Schlömann, A., 1892, 354). This reaction, which is a typical case of replacement in the benzene ring resulting from the lability of the methoxy-group of the trinitroanisole, may therefore be regarded as occurring in two phases: the first leads to the formation of the additive compound, and the second to that of picrylpiperidine, with elimination of methyl alcohol. Guye (A., 1910, ii, 699) and Wroczynski and Guye (*ibid.*) have developed the view that all substitution processes are preceded by the formation of additive compounds (compare Schmidlin and Lang, A., 1910, i, 836; 1912, i, 473), and Sudborough and Picton (T., 1906, **89**, 583) suggest that the intermediate compound is quinonoid in character (compare Meisenheimer, A., 1902, i, 795; Borsche, A., 1912, i, 180; Borsche and Bahr, A., 1914, i, 28). According to these views and to Thiele's theory of partial valencies, the reaction between trinitroanisole and piperidine may be interpreted as follows:



i*

Since resolution of the additive compound is difficult and is facilitated by the presence of alkali, the latter probably converts the OH into ONa, giving a salt more readily decomposable than the parent intermediate compound.

The s-*trinitroanisole–piperidine additive compound*,

$$C_7H_5O_7N_3,C_5H_{11}N,$$

crystallises in pale yellow, prismatic needles, beginning to decompose at about 281°.

The action of 1-chloro-2:4-dinitrobenzene on primary aromatic amines gives rise to nitro-derivatives of diphenylamine, and the equilibria of the binary systems formed of the chlorodinitrobenzene and *o*-nitroaniline, *m*-nitroaniline, *a*-naphthylamine, and *p*-aminoacetophenone have been investigated in order to ascertain if intermediate compounds are formed in these cases. These systems, except that formed by *m*-nitroaniline, give rise to additive compounds, which must be regarded as the first stage of the reaction yielding diphenylamine derivatives. The system 1-chloro-2:4-dinitrobenzene:*o*-nitroaniline yields an additive compound, m. p. about 35°; the eutectic between this compound and the chlorodinitrobenzene has m. p. 31° and corresponds with 22% of *o*-nitroaniline, whilst that between the compound and *o*-nitroaniline has m. p. 33·5° and corresponds with 45% of the chlorodinitrobenzene. The system 1-chloro-2:4-dinitrobenzene–*m*-nitroaniline shows only one eutectic (52% of *m*-nitroaniline; m. p. 34·3°). The system 1-chloro-2:4-dinitrobenzene–*a*-naphthylamine yields an additive compound (1 mol.:1 mol.), m. p. 71·5°, the eutectics between compound (1) and chlorodinitrobenzene, m. p. 38°, and (2) *a*-naphthylamine, m. p. 34°, corresponding with 12% and 77% of the amine. The system 1-chloro-2:4-dinitrobenzene–*p*-aminoacetophenone forms a labile additive compound (1 mol.:2 mols.), which undergoes dissociation; the whole system was not examined, since, when the amino-compound is in excess, heating brings about the following reaction:

$$C_6H_3Cl(NO_2)_2,2CH_3\cdot CO\cdot C_6H_4\cdot NH_2 = \\ CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2 + CH_3\cdot CO\cdot C_6H_4\cdot NH_2,HCl.$$

T. H. P.

6-Methylisatin. (MLLE) J. BONNEFOY and JH. MARTINET (*Compt. rend.*, 1921, **172**, 220—221).—*m*-Toluidine condenses with mesoxalic esters to give esters of 6-methyldioxindole-3-carboxylic acid, which when saponified in the air lose their carboxyl group, the dioxindole undergoes oxidation, and an alkali isatate is formed, which, when acidified, gives the free isatin.

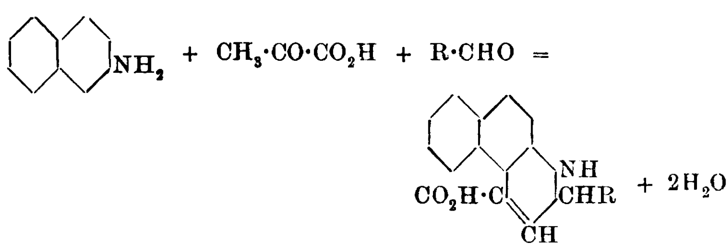
An alternative process is to act on *m*-toluidine with carbon disulphide in the presence of hydrogen peroxide and to treat the resulting di-*m*-tolylthiocarbamide with potassium cyanide and lead carbonate in aqueous alcohol. The *hydrocyanodi*-m-*tolylcarbondiimide*, m. p. 128°, thus obtained, when heated at 40° in benzene with aluminium chloride for four hours, yields 6-*methylisatin*-m-

toluidide, m. p. 65—67°, and from this, by the action of boiling dilute hydrochloric acid, 6-methylisatin is obtained. This isatin, when treated in acetic acid solution with the technical melt of phenylglycine, gives 3(2′)-*indoxyl*-6-*methylindole*, m. p. 307°.

W. G.

Doebner's Reaction. III. R. Ciusa and G. Zerbini (*Gazzetta*, 1920, **50**, ii, 317—326).—It has been shown previously (A., 1915, i, 894, 895) that the action of β-naphthylamine and benzaldehyde on pyruvic acid yields α-phenyl-β-naphthacinchonic acid, together with a hydrogenated acid as a secondary product. Such hydrogenated acids do not represent the sole secondary products of the reaction, since the use of piperonaldehyde or anisaldehyde in place of benzaldehyde results in the formation of the corresponding α-substituted tetrahydro-β-naphthacinchonic acids, together with appreciable proportions of methoxy- or methylenedioxy-benzyl-β-naphthylamine. When benzaldehyde is employed, the reaction yields benzyl-β-naphthylamine in small proportion, and a compound, $(C_{17}H_{14}N)_2$, m p. 167°, which is regarded as the lower melting isomeride of di-β-naphthyldiamino-derivative of *s*-dibenzyl, formed, along with the benzyl-β-naphthylamine, by the reduction of benzylidene-β-naphthylamine; the formation of this compound corresponds with the pinacone reduction of aldehydes effected by magnesium amalgam (Ciusa and Milani, A., 1914, i, 250). Reduction of benzylidene-β-naphthylamine by means of aluminium amalgam (Anselmino, A., 1908, i, 259) yields a compound, $C_{34}H_{28}N_2$, m. p. 220°, together with a small proportion of a compound, m. p. below 170°.

The origin of these hydrogenated compounds is explained by assuming the initial formation of a dihydrogenated acid:



(compare Simon, A., 1907, i, 241; Simon and Mauguin, A., 1907, i, 725), this acid then undergoing oxidation and reduction to a mixture of cinchonic and tetrahydrocinchonic acids.

α-Anisyl-β-naphthacinchonic acid (Doebner, A., 1894, i, 261, 532), obtained by the interaction of anisaldehyde, β-naphthylamine, and pyruvic acid, forms a *methyl* ester, $C_{20}H_{14}ON{\cdot}CO_2Me$, m. p. 145°, and an *ethyl* ester, m. p. 97°. The mother liquors from this acid yield: (1) α-anisyltetrahydro-β-naphthacinchonic acid, which crystallises in small, colourless needles, m. p. 234°, forms a *methyl*

ester, m. p. 144°, and a *sodium* salt, $C_{21}H_{18}O_3NNa,5H_2O$, and is oxidised to α-anisyl-β-naphthacinchonic acid by means of permanganate; (2) *p*-methoxybenzyl-β-naphthylamine, which, like the tetrahydrogenated acid, its methyl ester, and its sodium salt, exhibits blue fluorescence in alcoholic solution.

α-3:4-Methylenedioxyphenyl-β-naphthacinchonic acid (Doebner, *loc. cit.*), prepared from piperonaldehyde, β-naphthylamine, and pyruvic acid, forms a *sodium* salt ($+4\frac{1}{2}H_2O$) and a *methyl* ester, $C_{21}H_{12}O_4NMe$, m. p. 170°. The mother liquors from this acid yield: (1) the corresponding *tetrahydro*-acid, $C_{21}H_{17}O_4N$, m. p. 233°, which gives the non-hydrogenated acid when oxidised by permanganate; (2) *methylenedioxybenzyl-β-naphthylamine*,

$$C_{10}H_7\cdot NH\cdot CH_2\cdot C_6H_3{:}O_2{:}CH_2,$$

which forms pink scales, m. p. 119°, and gives a *platinichloride*.

αβ-Dinaphthyldiaminodibenzyl, $C_{34}H_{28}N_2$, obtained as a secondary product in the interaction of benzaldehyde, β-naphthylamine, and pyruvic acid, has m. p. 167°; its *isomeride* (see above) crystallises in colourless needles, m. p. 220°. T. H. P.

The Oxidation of Carbazole. WILLIAM HENRY PERKIN, jun., and STANLEY HORWOOD TUCKER (T., 1921, **119**, 216—225).

Condensation of Glycine Anhydride with Aldehydes. New Synthesis of *dl*-Phenylalanine and *dl*-Tyrosine. TAKAOKI SASAKI (*Ber.*, 1921, **54**, [*B*], 163—168).—Glycine anhydride condenses readily with aldehydes to yield 2:5-diketo-3:6-dialkylidenepiperazines, which are smoothly reduced and hydrolysed in one operation to amino-acids:

$$H_2C{<}{}^{CO\cdot NH}_{NH\cdot CO}{>}CH_2 + 2R\cdot CHO \longrightarrow$$

$$R\cdot CH{:}C{<}{}^{CO\cdot NH}_{NH\cdot CO}{>}C{:}CHR \longrightarrow 2R\cdot CH_2\cdot CH(NH_2)\cdot CO_2H.$$

2:5-*Diketo*-3:6-*dibenzylidenepiperazine*, pale yellow crystals, decomp. 298—300°, when rapidly heated, is obtained in 62% yield when a mixture of glycine anhydride, benzaldehyde, anhydrous sodium acetate, and acetic anhydride is heated for eight hours at 120—130°; under these conditions the imino-hydrogen atoms are not replaced by the acetyl group. The compound is converted by boiling hydriodic acid (D 1·7) in the presence of red phosphorus into *dl*-phenylalanine, leaflets, decomp. 263—264°, when rapidly heated, the yield being 83% of that theoretically possible; it is reduced by zinc dust in boiling glacial acetic acid to 2:5-*diketo*-3:6-*dibenzylpiperazine*, m. p. 290—291°, which may also be prepared by Willstätter's catalytic method, but less advantageously on account of the sparing solubility of both initial and final products in the usual media. Similarly, 2:5-*diketo*-3:6-*dianisylidenepiperazine*, decomp. above 300°, is transformed into *dl*-tyrosine. With *p*-hydroxybenzaldehyde, 3:6-*di*-p-*acetoxybenzylidene*-2:5-*diketopiperazine*, yellow crystals, decomp. above 300°, is produced,

which is likewise transformed into *dl*-tyrosine by the action of hydriodic acid and red phosphorus. H. W.

Condensation of certain Dipeptide Anhydrides with Benzaldehyde. TAKAOKI SASAKI and TOKUDJI HASHIMOTO (*Ber.*, 1921, **54**, [*B*], 168—171).—The behaviour of dipeptide anhydrides of which one component is the glycyl group, towards benzaldehyde has been investigated; as was to be expected, it is found that the condensation involves the introduction of a single benzylidene group into the molecule (compare preceding abstract). Simultaneously, one or more acetyl groups are introduced, and, since it has been shown that the glycyl imino-group is not affected under the experimental conditions adopted, it follows that acetylation must occur in the second component of the molecule. Unfortunately, optically active dipeptide anhydrides become almost or completely racemised during the process.

dl-Glycylalanylanhydride, benzaldehyde, sodium acetate, and acetic anhydride give 2:5-*diketo*-1-*acetyl*-3-*benzylidene*-6-*methylpiperazine*, $MeHC{<}{}^{NAc\cdot CC}_{CO-NH}{>}C{:}CHPh$, m. p. 163—164°; similarly, *dl*-glycyl-leucylanhydride gives 2:5-*diketo*-1-*acetyl*-3-*benzylidene*-6-iso*butylpiperazine*, m. p. 152—153°, whilst glycyl-*l*-tyrosine anhydride yields 2 : 5 - *diketo*-1-*acetyl*-2-*benzylidene*-6-p-*acetoxybenzylpiperazine*, m. p. 153—154°. H. W.

[Derivatives of Hydrosulphamine.] A Correction. A. BINZ and E. HOLZAPFEL (*Ber.*, 1921, **54**, [*B*], 178. Compare this vol., i, 30).—Azosulphimcarbohydrosulphide, benzenylazosulphimcarboanilide, $Ph\cdot C{<}{}^{N\cdot S}_{\quad N}{>}C\cdot NHPh$ (Tiemann, A., 1891, 557), and dibenzenylazosulphime (von Hofmann and Gabriel, A., 1892, 1109) must be considered as derivatives of hydrosulphamine. The discovery of benz*iso*thiazole is due to Gabriel and Posner, and not to Bamberger, as erroneously given. H. W.

***p*-*iso*Nitriloazobenzene [*p*-Carbylaminoazobenzene.]** M. PASSERINI (*Gazzetta*, 1920, **50**, ii, 340—344).—When heated in alcoholic (about 80%) solution with chloroform and sodium hydroxide, *p*-aminoazobenzene, like other primary amines, is converted into the corresponding carbylamine in about 80% yield.

p-*Carbylaminoazobenzene*, $NPh{:}N\cdot C_6H_4\cdot N{:}C$, crystallises in mammillary masses of slender, yellow needles, which begin to turn brown at 106°, m. p. 110°. It is more stable than many other carbylamines, but yields carbon monoxide and *p*-aminoazobenzene when boiled with a mineral acid. When boiled with concentrated acetic acid it gives acetyl-*p*-aminoazobenzene (compare Schultz, A., 1884, 902), and by boiling aqueous oxalic acid (compare Guillemard, A., 1908, i, 718) it is converted into formyl-*p*-aminoazobenzene (compare Betti, A., 1898, i, 656). When oxidised in ethereal solution by means of yellow mercuric oxide it yields a mixture of amorphous

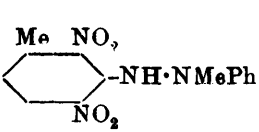
substances, from which the expected *p*-carbimidoazobenzene (compare Gautier, *Ann. Chim. Phys.*, 1869, [iv], **17**, 203) could not be isolated; in wet ether, however, this oxidation causes evolution of carbon dioxide and formation of 4:4′-carbamidoazobenzene, $(NPh:N\cdot C_6H_4\cdot NH)_2CO$ (compare Berju, A., 1884, 1148). Oxidation of *p*-carbylaminoazobenzene in acetone solution by means of hydrogen peroxide gave no result. Treatment with peracetic acid in acetone solution yields: (1) a *compound* crystallising in shining, ochre-yellow scales, m. p. 270—280°; (2) a *compound* forming shining, orange-yellow prisms, m. p. 195—198°; and (3) as principal product, a *compound* crystallising in refractive, yellow plates, m. p. 147—148°; to none of these three has a formula been assigned. A solution of *p*-carbylaminoazobenzene in the minimal proportion of benzaldehyde gradually deposits an *additive* compound of 2 mols. of the aldehyde to 1 mol. of the carbylamine, this forming pale yellow crystals, m. p. 222—223°. Similarly, salicylaldehyde furnishes a crystalline *compound*, m. p. about 150° (crude). These investigations are to be completed. T. H. P.

Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. IV. Additive Compounds of Thiocarbamide with Azonium Iodides. BAWA KARTAR SINGH and MIRI LAL (T., 1921, **119**, 210—211).

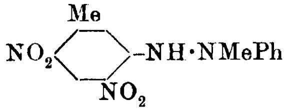
Arylazoglyoxalinecarboxylic Acids. ROBERT GEORGE FARGHER (T., 1921, **119**, 158—164).

Aromatic Nitro-derivatives. XII. Action of *as.*-Phenylmethylhydrazine on β- and γ-Trinitrotoluenes. M. GIUA (*Gazzetta*, 1920, **50**, ii, 327—330. Compare A., 1920, i, 100).—By the interaction of *as.*-phenylmethylhydrazine on *s.*-trinitroanisole, the author obtained 2:4:6-trinitro-*N*′-methylhydrazobenzene (A., 1920, i, 99), which is isomeric with the compound obtained by Knorr and Weidel (A., 1909, i, 965) from *s.*-phenylmethylhydrazine and picryl chloride. The author has now studied the action of *as.*-phenylmethylhydrazine on 2:3:4- and 3:4:6-trinitrotoluenes, in which, according to the results of Hepp (A., 1883, 315) and Will (A., 1914, i, 509), the nitro-group in the meta-position to the methyl group is readily substituted; these reactions yield the substituted hydrazo-compounds, which are orange-yellow and are somewhat more stable than the corresponding hydrazo-compounds, and melt without decomposition.

*α-Phenyl-β-2:4-dinitro-*m*-tolyl-α-methylhydrazine* (annexed formula), obtained from 2:3:4-trinitrotoluene and *as.*-phenylmethylhydrazine, forms orange-yellow prisms, m. p. 147°, and gives a dark yellow coloration with concentrated sulphuric acid and a green coloration changing to reddish-brown when its alcoholic solution is treated with an alkali.



*α-Phenyl - β - 4 : 6 - dinitro-*m*-tolyl-α-methylhydrazine* (annexed formula), obtained from 3 : 4 : 6-trinitrotoluene and *as.*-phenylmethylhydrazine, forms shining, orange-yellow, prismatic plates, m. p. 141°, and gives a yellowish-brown coloration with concentrated sulphuric acid and a reddish-brown coloration when treated in alcoholic solution with an alkali.



The compound, m. p. 150° (decomp.), regarded by the author as a benztriazole derivative (A., 1920, i, 100), may be identical with the compound decomposing at 110—176° described by Borsche and Fiedler (A., 1913, i, 842). T. H. P.

Protein Chemistry. I. The Capacity of Combining with Iodine and the Constitution of the Proteins. F. Blum and E. Strauss (*Zeitsch. physiol. Chem.*, 1921, **112**, 111—166).—From a number of experiments carried out in order to study the nature of the chemical combination of iodine with the proteins, the following conclusions are derived: Iodine entering into combination with proteins is not attached to the carbon ring only, but is also taken up by the imino-groups. The latter iodine is easily removed from the compound by reduction with sulphur dioxide. The *N*-iodine was observed to be in a constant relation to the *C*-iodine. In the action of iodine on proteins, substitution and oxidation take place, involving the loss of a biuret group and alteration in the tryptophan and cystine complexes. In the case of partial iodation, the iodated proteins thus obtained contain *C*-iodine, but no *N*-iodine, and do not give the biuret reaction on degradation with alkali; the tryptophan and the cystine groups are unaltered under these conditions. The introduction of the iodine into the molecule, and the heating of the protein after the removal of the *N*-iodine, makes the protein resistant to peptic digestion. S. S. Z.

The Free Amino-groups of the Proteins. III. S. Edlbacher (*Zeitsch. physiol. Chem.*, 1920, **110**, 153—155); J. Herzig (*ibid.*, 156—157).—A discussion of the results obtained by the action of methyl sulphate on proteins. S. S. Z.

The Free Amino-groups of the Proteins. S. Edlbacher (*Zeitsch. physiol. Chem.*, 1921, **112**, 80—85).—Casein was methylated with methyl sulphate, hydrolysed, and the *N*-methyl value determined in the various fractions. The results obtained were as follows: *N*-methyl value of the monoamino-acid fraction = 0; of the histidine–arginine fraction = 7·5; of the lysine fraction = 73·4. S. S. Z.

Limits of the Precipitation of Mucin by Acids and by Zinc Salts. L. Dejust (*Bull. Soc. chim. biol.*, 1920, **2**, 208—210).—The mucin employed for this investigation was prepared from the sub-maxillary glands of oxen by extraction with 0·5% potassium

hydroxide, and acidification of the extract with acetic acid. The mucin, after two reprecipitations, was washed with alcohol and ether. It contained 13·69% of nitrogen. The precipitation of mucin from solution by acids and zinc salts was studied.

J. C. D.

Protein Chemistry. II. Iodoglobin. EDUARD STRAUSS and RUDOLF GRÜTZNER (*Zeitsch. physiol. Chem.*, 1921, **112**, 167—175).—Globin was iodated, and it was found that the iodine entered the molecule both as *C*-iodine and *N*-iodine (see preceding page). On reducing the *N*-iodine with sulphur dioxide and treating the protein again with iodine, the original iodine value was obtained. There was a great inhibition in the peptic action on the fully iodated protein. Protection was also observed in the *C*-iodine compound when it was suspended in water after being heated.

S. S. Z.

Hæmatoporphyrin. V. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1920, **109**, 125—140).—The dimethyl ester of hæmatoporphyrin, $C_{36}H_{42}O_6N_4$, was prepared. It can be extracted with ether. The *copper* salt, $C_{36}H_{40}O_6N_4Cu$, was obtained as clusters of needles by mixing solutions of the ester and of copper sulphate in glacial acetic acid. The *diethyl ether* of hæmatoporphyrin, $C_{34}H_{34}O_6N_4Et_2,2MeOH$, when prepared from chlorohæmin by treatment with a solution of hydrobromic acid, formed crystals from methyl alcohol, m. p. 118—119°, and did not yield an ethyl ester, but the diethyl ether, when prepared from β-bromohæmin, in contradistinction to that just described, had no definite melting point; the hydrochloric acid compound crystallised in conglomerates of needles. The pure diethyl ether, on treatment with ethyl alcohol, even at the boiling point, gave rise to a substance isomeric with the di-ether. It is assumed that the di-ether has a betaine-like structure. Finally, the pure diethyl ether gave an *ethyl* ester, m. p. 91—93° (not sharp), on treatment with absolute alcohol and dry hydrogen chloride for twenty minutes at the ordinary temperature. By the action of aniline on the mixture of the dihydrobromide of the hydrobromohæmatiporphyrin ester, four fractions were obtained, which were not hæmatoporphyrin derivatives, but substituted hæmines.

S. S. Z.

A "Coupled" Nucleic Acid from the Pancreas. I. EINAR HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1920, **109**, 141—165).—The author has isolated from the pancreas a nucleic acid which is a compound of guanylic acid with a tetranucleotide, and is similar to that described by Feulgen (compare this vol., i, 70). It was prepared in the following way: the dried pancreas was treated with very weak hydrochloric acid (0·06*N*) in the cold, and the residue was then extracted with alkali at 0° and precipitated with hydrochloric acid. By treating the nuclein solution with calcium chloride, the nucleic acid was obtained. From the calcium salt, the free acid and the calcium–sodium salt were prepared. The

three preparations gave a quotient $N/P=1\cdot88$, which corresponds with the quotient for a compound consisting of two molecules of guanylic acid and one molecule of a tetranucleotide acid.

S. S. Z.

Yeast-Nucleic Acid. S. J. THANNHAUSER and P. SACHS (*Zeitsch. physiol. Chem.*, 1920, **109**, 177—182).—A reply to Steudel and Peiser (this vol., i, 66). Böhringer's yeast-nucleic acid was shaken for twenty-four hours with water, the filtrate concentrated under diminished pressure, and boiled with brucine, after which it was dissolved in hot alcohol. No precipitate of the brucine salt of uridinephosphoric acid was formed. It is therefore concluded that the yeast-nucleic acid in question does not contain free uridinephosphoric acid, and that the barium salt obtained by Steudel and Peiser by fractionating the yeast-nucleic acid with barium acetate is not that of uridinephosphoric acid. S. S. Z.

Nuclein Metabolism. X. The Deamidisation of Triphosphonucleic Acid. S. J. THANNHAUSER and P. SACHS (*Zeitsch. physiol. Chem.*, 1921, **112**, 187—192).—The mixture of acids (triphosphonucleic acid and mononucleotides) obtained by mild ammoniacal hydrolysis of yeast-nucleic acid was deaminised by treating the mixture, dissolved in acetic acid, with sodium nitrite, neutralising, and precipitating with lead acetate. The lead compound was decomposed with hydrogen sulphide, filtered, the filtrate concentrated in a vacuum, and precipitated with alcohol. By treatment with brucine and fractional crystallisation, two crops of crystals were obtained melting at 189—190° and 194—195° respectively, but these gave on analysis identical figures corresponding with those required for the brucine salt of a deaminotriphosphonucleic acid. The pure triphosphonucleic acid was deaminised in the above way, and the brucine salt prepared from it melted at 185°. The adenosine phosphoric acid could not be deaminised without being decomposed. S. S. Z.

The Demonstration of Pyrrole Compounds in the Proteins. N. TROENSEGAARD (*Zeitsch. physiol. Chem.*, 1921, **112**, 86—103).—The author advances a theory that the protein molecule is composed mostly of heterocyclic compounds, and in substantiation of it has endeavoured to demonstrate the presence of pyrrole substances in gliadin and gelatin. To avoid the decomposition of the pyrrole compounds, the author did not use solvents which contained water, and, further, stabilised the pyrrole groups by introducing an acid radicle. The gliadin was dissolved in methyl-alcoholic potassium hydroxide which was free from water. It was then neutralised, concentrated in a vacuum, and acetylated with anhydrous sodium acetate and acetic anhydride. The acetylated product was dissolved in anhydrous acetic acid and treated with glacial acetic acid–hydrogen iodide on the water-bath. No melanin was formed. The pyrrole compounds were obtained by distilla-

tion with superheated steam. The dry gelatin was dissolved in anhydrous methyl-alcoholic potassium hydroxide, neutralised with acetic acid, treated with amyl alcohol, the methyl alcohol removed by distillation, and the pasty residue treated with amyl alcohol and sodium, and then with carbon dioxide, and, after adding water, extracted with ether. The latter and the amyl alcohol were then distilled off, leaving the pyrrole substances behind.

S. S. Z.

The Preparation of Highly Active Saccharase (Invertase) Preparations. II. OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **109**, 65—98. Compare A., 1920, i, 689, 896).—Highly active saccharase preparations were made by autolysing yeast submitted to a preliminary treatment, extracting the yeast residues with water, and fractionating with alcohol. Protein was removed from the enzyme solutions thus obtained by treatment with kaolin. Such saccharase solution passed through a Chamberland filter and a collodion membrane. By dialysis, a purer preparation was obtained, and a loss of 50% of the enzyme was incurred in this manipulation. The nitrogen content of the preparation, however, fell from 4% to 1·2%. S. S. Z.

Preparation of Highly Active Saccharase (Invertase) Preparations. IV. OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1921, **112**, 104—110).—A separation of saccharase from yeast gum by filtration through a membrane could not be effected. This observation coincides with Euler and Fodor's assumption that there is a relationship between the two substances. No improvement in the purity of the enzyme was observed when it was filtered through the membrane instead of being dialysed. S. S. Z.

Toxic Actions in Enzymic Processes. IV. Electromotive Measurements of the Combination of Silver and Copper with Saccharase and other Organic Compounds. H. VON EULER and OLOF SVANBERG (*Fermentforsch.*, 1920, **4**, 142—183; from *Chem. Zentr.*, 1921, i, 154. Compare A., 1920, i, 689; this vol., i, 68, 81).—It has been shown previously that silver becomes de-ionised by the formation of complex compounds with saccharase. Numerous substances have now been comparatively examined electrometrically in order to ascertain whether any of them possesses an approximately similar affinity for silver ions. This is found to be the case with egg-albumin (Sörensen), cysteine, and a nucleic acid, so that it would appear that the action of the saccharase molecule is due to the presence of the SH group and the components of the nucleic acid; it is shown that these have much less affinity for the cupric than for the silver ion, and the lower toxicity of copper salts towards saccharase is thereby explained.

The paper concludes with a summary of the results described in the four communications. H. W.

The Direct Synthesis of Carbamide by Urease. TH. J. F. MATTAAR (*Rec. trav. chim.*, 1921, **40**, 65—66); H. P. BARENDRECHT (*ibid.*, 66).—Polemical. A continuation of the discussion on this subject, see A., 1920, i, 537, 826. W. G.

Physiological Chemistry.

The Mechanism of the Toxic Action of Aromatic Nitro-compounds. The Respiration Problem of Animal and Plant Cells. WERNER LIPSCHITZ (*Zeitsch. physiol. Chem.*, 1920, **109**, 189—258).—Living cells in the process of respiration remove the oxygen from nitro-compounds and reduce them to hydroxylamine compounds. In contradistinction to the nitro-compounds, these substances are powerful blood toxins. They change hæmoglobin into methæmoglobin. Experiments instituted with the object of elucidating the mechanism of the reaction are described.

S. S. Z.

The Prosthetic Group of Blood Pigments. II. The Influence of Age on the Blood Pigment. WILLIAM KÜSTER (*Biochem. Zeitsch.*, 1920, **109**, 117—124).—Hæmin was prepared from the blood of an old horse and from that of an old bullock. The mono- and di-methyl and the ethyl esters were prepared. The hæmins from the old animals resembled one another in one main point, namely, that one of the carboxyl groups did not react with hydroxylamine, which suggests that they did not contain the ferrichloride group. S. S. Z.

Detection of Formic Acid in Human Blood. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1920, **109**, 99—107).—Formic acid was detected in the blood of normal individuals and patients suffering from nephritis. In the blood of diabetics, formic acid was found in some cases, but not in others. One of the negative results was given by the blood of a diabetic patient with the highest sugar content. This suggests that the formic acid is not formed as an artificial product from the sugar in the blood during the estimation, but is actually present there before it is manipulated. The mercuric chloride and Fenton and Sisson's methods for the detection of formic acid were used. S. S. Z.

Physiological Significance of Formic Acid. A. SLOSSE (*Bull. Soc. chim. biol.*, 1920, **2**, 150—156).—Estimations of formic acid in urine and blood indicate that this substance represents a definite stage in the katabolism of many substances. J. C. D.

A Comparison of the Action of Benzene and *cyclo*Hexane on the Formed Elements of the Blood. L. LAUNOY and M. LÉVY-BRUHL (*Bull. Soc. chim. biol.*, 1920, **2**, 145—149).—*cyclo*Hexane is some three times less toxic than benzene, and does not show the leucotoxic action so characteristic of the latter substance. J. C. D.

Arrest of Glycolysis [in Blood] by a Mixture of Sodium Fluoride and Monopotassium Phosphate. L. AMBARD (*Bull. Soc. chim. biol.*, 1920, **2**, 202—203).—The author advises the use of a mixture of 1 part of sodium fluoride and 2 parts of potassium dihydrogen phosphate in the proportion of 15 grams per litre of blood. J. C. D.

Estimation of Carbon Monoxide in the Blood, and Determination of the Maximum Absorption of Carbon Monoxide by the Blood. MAURICE NICLOUX (*Bull. Soc. chim. biol.*, 1920, **2**, 171—179).—The method and apparatus are described in detail. The carbon monoxide is converted into carbon dioxide by explosion with oxygen, and estimated as such. Blood saturated with carbon monoxide took up from 25·55 to 23·45 vols. %, and when submitted to the action of a mixture of carbon monoxide and 5% of nitrogen the percentage volume of the former gas taken up by the blood was found to be from 23·5 to 21·5. J. C. D.

Action of Glycerol. II. Action of Glycerol on the Blood. ITALO SIMON (*Arch. Farm. sper. Sci. aff.*, 1920, **30**, 53—64, 77—80, 81—96, 102—112. Compare A., 1916, i, 448).—Subcutaneous injection into rabbits of a single quantity of glycerol sufficient to produce hæmoglobinuria causes modifications of the blood similar to those resulting from the withdrawal of a considerable amount of blood. Repeated injections at short intervals of smaller quantities give rise to irritation of the lymphatic tissue, in addition to the effects of repeated small withdrawals of blood and to the entry into circulation of substances derived from the destruction of the red corpuscles and elements of the subcutaneous tissue. T. H. P.

Colloidal Chemical Action of Salts of the Alkali Metals on the Process of Phagocytosis. W. RADSMA (*Arch. Néerland physiol.*, 1920, **4**, 197—215).—The effect is a lyotropic action on the membrane of the leucocyte, and does not depend on the formation of protein ions, or on an action on the interior of the leucocyte. For anions the intensity of phagocytosis diminishes in the order Cl, ClO_3, Br, NO_3, I, CNS, and for kations in the order Na, K, Rb, Cs, Li. G. B.

Serologic Behaviour of Different Races of Amœbæ. W. VON SCHUCKMANN (*Arb. Gesundh.-Amt.*, 1920, **52**, 133—162; from *Chem. Zentr.*, 1921, i, 111).—Breeding experiments, morphological and cultural behaviour, and immunising experiments are

described. The action of an amœbic immune serum on a homologous race of amœbæ is accompanied by a more or less pronounced clotting of the now immobile amœbæ, which, however, is not permanent, since mobility is recovered gradually. The flagellate forms produced by certain races of amœbæ are also specifically influenced by an immune serum prepared with the corresponding amœbæ.

H. W.

Influence of Bile and Bile Salts on the Most Important Digestive Ferments. J. TEMMINCK GROLL (*Ned. Tÿdschr. Geneeskunde*, 1920, **64**, 1157—1168; from *Chem. Zentr.*, 1920, iii, 935—936).—In order to eliminate the effects due to varying alkalinity, a phosphate buffer mixture giving a constant P_H was added to the solutions containing bile and to the control solutions. Pancreas amylase becomes increasingly activated by bile in concentrations of 0·06% to 6% Saliva amylase is activated by very slight concentrations of bile (about 0·1%); in medium concentration the latter is without effect, but exerts a restrictive action if present to the extent of more than 5%. It does not appear to influence the action of the lipases on solutions of triacetin or monobutyrin. The marked acceleration of the fission of oils seems to depend on the better emulsification of the latter in the presence of bile salts. Proteases and pepsin do not act on fibrins if P_H is smaller than 3·1; bile therefore has a restrictive action.

[With C. N. VAN DER MEER.]—In the case of trypsins, bile does not appear to have any direct influence on the fermentative fission of amino-acids, which, however, it accelerates by altering the coagulated proteins. H. W.

Activity of the Kidneys and Acidic Basic Equilibrium. T. NAGAYAMA (*Amer. J. Physiol.*, 1920, **51**, 434—448; from *Chem. Zentr.*, 1921, i, 52).—The amount of urea eliminated in an hour divided by the quantity present in 100 c.c. of blood was estimated for fifteen rabbits after administration of 5 grams of urea. Control experiments were made with solutions containing 0·5 gram $NaH_2PO_4,4H_2O$ and 2·32 grams $Na_2HPO_4,2H_2O$ ($p_H = 7·48$) and 3 grams $NaH_2PO_4,4H_2O$ and 2·81 grams $Na_2HPO_4,2H_2O$ in water (35 grams in either case). Elimination of urea was diminished by the acid phosphate, and the carbon dioxide content of the plasma was lower. Slight increase of the latter was observed with alkaline phosphate and the activity of the kidneys was normal. Administration of sodium hydrogen carbonate, which sensibly increased the carbon dioxide, caused a very slight decrease in the elimination of urea. H. W.

Elimination of Urea and of Phosphates by the Kidneys. T. NAGAYAMA (*Amer. Journ. Physiol.*, 1920, **51**, 449—453; from *Chem. Zentr.*, 1921, i, 52. Compare preceding abstract).—The simultaneous presence of a neutral mixture of phosphates increases the elimination of urea by the kidneys. H. W.

An Investigation of the Fats of the Gonads of *Rhizostoma Cuvieri*. FELIX HAUROWITZ (*Zeitsch. physiol. Chem.*, 1920, **112**, 28—37).—The gonads were dehydrated with ammonium sulphate and extracted with 96% alcohol and with ether. On removing the solvent the fat was obtained which formed about 9·4% by weight of the original material. The fat gave the following figures: D 0·9606; acid number, 52·2; saponification number, 190·7; Hehner's number, 83·7; iodine number, 110·4; Reichert-Meissl number, 2·6; neutralising number for the water-soluble acids of 5 grams, 60·0. The fat contained 0·542% of nitrogen, 0·335% of phosphorus, and 2·87% of chlorine. Bromine, iodine, and sulphur were absent; the unsaponifiable portion was 2·9% of the total fat. Hydrocarbons were absent. The presence of cholesterol and cetyl alcohol was established. Amongst the fatty acids formic, *n*-octoic, myristic, palmitic, and linolic were identified; oleic and hydroxy-fatty acids were absent. In the unsaponifiable portion, choline, trimethylamine, and phosphoric acid in the free condition, as well as in combination with organic compounds, were found. S. S. Z.

Is Selenium Present in the Animal and the Plant Organisms? R. FRITSCH (*Zeitsch. physiol. Chem.*, 1920, **109**, 186—188).—Polemical. A reply to Gassmann, A., 1918, ii, 309.

S. S. Z.

Normal Thiocyanate Content of the Body. L. CHELLE (*J. Soc. Pharm. Bordeaux*, 1920, **58**, 20—54; from *Chem. Zentr.*, 1921, i, 100).—The author finds that the following amounts, calculated as thiocyanic acid, are present; in the saliva (10 samples), 17·3—217 mg.; in urine (10 samples), 0—6·59 mg.; in gastric juice (1 sample), 7·08 mg. per litre. The substance is not present in pancreatic juice, milk, or blood, but in a case of carbon monoxide poisoning 12·39 mg. were found in the latter. H. W.

The Urinary Elimination of the Hydrochloride of Diethylaminoethyl *p*-Aminobenzoate (Novocaïne, Syncaïne, etc.). R. THIEULIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 463—466).—After intramuscular injection of syncaïne hydrochloride into a rabbit it was possible to detect both syncaïne itself and its products of hydrolysis, *p*-aminobenzoic acid and diethylaminoethyl alcohol, in the urine during the succeeding twenty-four hours. During the three days following the injection there was an increase in the amino-acids and ammonia excreted in the urine. W. G.

Substances which Form Acetone in Urine and the so-called Physiological Acetonuria. EMILIO PITTARELLI (*Rif. med.*, 1920, **36**, 303—306; from *Chem. Zentr.*, 1921, i, 111—112).—A substance is present in urine which combines with acetone and thus masks the presence of the latter. The existence of this substance explains the negative result of the acetone test in a urine which yielded acetone when distilled. Free acetone is never

present in urine, which, however, contains a substance yielding acetone. A physiological acetonuria, in the sense that every urine contains minimal amounts of acetone, is not existent.

H. W.

The Behaviour of some Pyrimidine Derivatives containing Sulphur in the Animal Organism. R. FREISE (*Zeitsch. physiol. Chem.*, 1920, **112**, 45—52).—On feeding thiouramil and the ammonium salt of thio-ψ-uric acid to dogs, a part of these compounds goes through the organism unchanged, whilst the other part is degraded, with the removal of the SH group. In the case of the thiouramil, about 49% of the substance undergoes cleavage during the passage, of which about a half is excreted as neutral sulphur, whilst the remainder leaves the body as sulphates. About 86% of the thio-ψ-uric acid is degraded in the organism, of which 14% is excreted as neutral sulphur and the remainder as sulphates.

S. S. Z.

The Toxicity and Skin Irritant Effect of certain Derivatives of $\beta\beta'$-Dichlorodiethyl Sulphide. E. K. MARSHALL, jun., and JOHN W. WILLIAMS (*J. Pharm. Expt. Ther.*, 1920, **16**, 259—272). —A number of these substances were tested on mice for toxicity, and the results indicate that the compounds containing halogens are the most toxic, and those containing aliphatic radicles in place of the chlorine are more toxic than those containing aromatic nuclei. The sulphones are more toxic than the corresponding sulphides. Other relative toxicities are recorded.

The toxicity of $\beta\beta'$-dichlorodiethylsulphoxide and $\beta\beta'$-dichlorodiethylsulphone, whilst of the same magnitude for mice, is markedly different for unicellular organisms, the latter being a hundred times more toxic than the former.

The solubilities of certain of the derivatives in water and xylene, as well as their rapidity of hydrolysis to yield an acid, have been determined. An attempt to correlate these results with the physiological action of the substances indicates that the theory of intracellular acid production by the action of mustard gas is probably correct.

J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Simple Method for the Automatic Registration of Production of Gas by Bacteria in Cultures and of the Absorption of Oxygen by Aerobic Bacteria which do not form Gas. ALEXANDER FLEMING and FRANCIS J. CLEMENGER (*Brit. J. Expt. Path.*, 1920, **1**, 66—69; from *Chem. Zentr.*, 1921, ii, 98—99).—In the case of anaerobic cultures, the mixture is

placed in a test-tube and covered with a layer of molten vaselin (4 parts) and paraffin (1 part). The latter subsequently solidifies, but prior to this there is inserted in the middle of it a small wooden disk, which is attached by a thread to the self-recording instrument. Evolution of gas lifts the paraffin plug, the movement of which is automatically recorded. The amount of carbon dioxide in the gaseous mixture can be estimated by absorption of the latter by sodium or potassium hydroxide solution. Similarly, if the plug is placed in the tube in such a manner that a column of air is left above the culture medium, it is possible to measure accurately the absorption of oxygen in the case of aerobic cultures by the descent of the plug in the tube. H. W.

Influence of the Reaction of Media and of the Presence of Buffer Salts on the Metabolism of Bacteria. C. G. L. Wolf (*Brit. J. Expt. Path.*, 1920, **1**, 288—309).—Two per cent. disodium hydrogen phosphate in glucose peptone inhibits or delays gas production by *Bacillus coli*, *B. welchii*, *B. sporogenes*, *B. histolyticus*, and *Vibrion septique*. The effect on the nitrogen metabolism is not pronounced. In the case of the saccharolytic organisms, the acid production is increased in the presence of buffer salts. Sodium phosphate increases the potency and stability of the toxin formed by *V. septique*. Potassium hydrogen phthalate and sodium pyrophosphate were also examined. The latter salt has not been previously used for this purpose; it may change by acids either to the orthophosphate or to the disodium dihydrogen pyrophosphate; its buffer action probably depends on the latter change. G. B.

Nitrogen Fixation by Cowpeas and Nodule Bacteria. Albert L. Whiting and Warren R. Schoonover (*Soil Sci.*, 1920, **10**, 411—420).—The earliest date at which nitrogen fixation was detected in inoculated cowpeas grown in purified nitrogen-free sand was nine days after planting. The progress of nitrogen fixation was related to the development of the plant. The more rapidly the plant grew, the greater was the rate of increase of nitrogen fixed. A rapid increase occurred soon after the time of development of the third leaf (first real leaf), which was about nineteen days after planting, and by the twenty-sixth day the nitrogen fixed was three times that contained in the seeds planted. W. G.

Influence of Luminous Radiations on *Azotobacter*. E. Kayser (*Compt. rend.*, 1921, **172**, 183—185. Compare this vol., i, 79).—A comparison of the influence of light of different colours on the third and sixth generations of *Azotobacter*. The total quantity of nitrogen fixed is always greater with the third generation, but considerable variations are shown, according to the colour of the radiation. The amount of nitrogen fixed per unit of carbohydrate decomposed is a minimum in yellow light. Except in blue light, the proportion of dextrose destroyed is always higher for the third generation. W. G.

Oligodynamy of Silver. III. R. DOERR (*Biochem. Zeitsch.*, 1921, **113**, 58—69. Compare A., 1920, 793, 794).—Silver inactivated by heating to red heat regains its oligodynamic activity when exposed to the atmosphere. If it is placed in melted paraffin, this regeneration does not take place. The oligodynamic action is due to the formation of soluble silver compounds on the surface of the metal through atmospheric oxidation. A certain surface of silver imparts a definite oligodynamic action to a volume of water, and this action diminishes owing to the fact that the soluble substances on the surface diffuse, and only by the introduction of a piece of silver with a surface covered with the soluble substances can the oligodynamic action be renewed. The metallic silver evidently does not go into solution. Typhoid, paratyphoid-*A*, and paratyphoid-*B* bacilli form colonies on agar plates at a certain distance from the silver, and behave under these conditions almost like *B. coli*. On the addition of lactose, on the other hand, the difference in the distance is more marked in the case of *B. coli*, and the author utilised this phenomenon to isolate *B. coli* from a mixture of the organisms. In some instances the author has also succeeded in suppressing the growth of *B. coli* in the mixture by means of the oligodynamic action of silver in a fluid medium, but this needs further investigation. S. S. Z.

The Chemical Mechanism of the Assimilation of Carbon Dioxide by Green Plants. P. MAZÉ (*Compt. rend.*, 1921, **172**, 173—175. Compare this vol., i, 151).—On the assumption that hydroxylamine is an intermediate product in the reversible conversion of nitric acid to ammonia, and thus formed in plants, the author proposes the following mechanism of the assimilation process. The hydroxylamine, acting as a base, fixes carbon dioxide, giving a compound, $CO_2,NH_2{\cdot}OH$, which may decompose as follows, $2CO_2,NH_2{\cdot}OH = OH{\cdot}CH_2{\cdot}CHO + HNO_2$, and both these compounds have been obtained from leaves of different plants. The glycollaldehyde may undergo reduction to give acetaldehyde, from which lactaldehyde may be obtained,

$$CH_3{\cdot}CHO + CO_2,NH_2{\cdot}OH = CH_3{\cdot}CH(OH){\cdot}CHO + NH_2{\cdot}OH,$$

and from these other compounds may be built up. All these changes will derive their necessary energy from the process of respiration. For the processes of nitrification, the author conceives the changes $2CO_2,NH_2{\cdot}OH = OH{\cdot}CH_2{\cdot}CHO + HNO_2$ and

$$6HNO_2 + 2H_2O + 2CO_2 + O_2 \longrightarrow 2CO_2,NH_2{\cdot}OH + 4HNO_3 + O_2$$
$$\longrightarrow 6HNO_3 + OH{\cdot}CH_2{\cdot}CHO.$$

W. G.

Action of Neutral Salts on the Resistance to Acids, Permeability, and Life of Protoplasts. WIDAR BRENNER (*Ber. deut. bot. Ges.*, 1920, **38**, 277—285).—The experiments here described were carried out with the epidermal and hypodermal cells of the leaves of the ordinary red cabbage, the anthocyanin of which served as indicator. As a criterion of the life of the cells, use was made of their ability to undergo normal plasmolysis or deplasmolysis. Solutions were prepared of sodium chloride,

potassium nitrate, chloride and sulphate, magnesium nitrate, chloride and sulphate, and calcium nitrate and chloride of such concentrations as to produce equally strong plasmolysis. After immersion in these solutions of the sections for twenty minutes, the plasmolysis having then reached its maximum, the sections were immersed for four hours in the same salt solutions containing hydrochloric acid in concentrations varying from 0·01 to 0·0005 mol. Deplasmolysis was then carried out in salt solutions of one-half and one-quarter the original concentration, and finally in water. In the magnesium sulphate and calcium chloride solutions, the concentration of hydrochloric acid withstood by the protoplasts was 0·004 mol., and in the sodium chloride and magnesium nitrate solutions 0·001 mol. Measurements of the hydrogen-ion concentrations of the solutions concerned show that in presence of calcium chloride, magnesium chloride, calcium nitrate, and potassium chloride, the protoplasts are able to resist 6, 3·5, 2, and 1·5 times, respectively, as many hydrogen ions as in absence of these salts. The toxicity of the hydrogen ions is not influenced by the presence of sodium chloride, magnesium nitrate or sulphate, or potassium nitrate. Noteworthy is the observation that addition of potassium sulphate appears to raise the toxicity of hydrochloric acid to double that conditioned by the hydrogen-ion concentration; for this, no explanation is advanced.

The change of colour, indicating penetration of hydrochloric acid into the cells, appears in very different times and with very different concentrations of acid, according to whether the salt influences the toxicity of the acid or not; the penetration is intimately connected with the activity of the hydrogen ions. The permeability of the plasma for the natural colouring matter of the cell is, however, in many cases very markedly influenced by neutral salts.

As regards the life of the protoplasts, magnesium salts, particularly the nitrate, are highly injurious; salts of the alkali metals behave similarly. The cells are, however, extremely tolerant towards calcium salts, in presence of which they show themselves capable of considerable regulation of the osmotic pressure; this phenomenon must be due to absorption and expulsion of the calcium salt. In a balanced solution having a composition similar to that of sea-water, but of greater concentration, the cells undergo rapid plasmolysis, but this disappears in the course of a few days and the tissues remain long alive. T. H. P.

Enzymatic Investigations of certain Green Algæ. KNUT SJÖBERG (*Fermentforsch.*, 1920, **4**, 97—141; from *Chem. Zentr.*, 1921, i, 153—154).—The very considerable influence of nutriment on the formation of enzymes has been examined at the instances of *Ulothrix zonata*, *Cladophora glomerata*, *Cl. fracta*, and *Spirogyra*. Amylase is decreased in culture solutions which contain sucrose, lactose, maltose, dextrose, or galactose, but is slightly increased in those containing starch, calcium tartrate, or calcium lactate. Potassium chloride or phosphate is without influence. Pre-treatment of

the algæ with alcohol (96%) increases the amylase action (the maximum is attained in three hours after treatment), and a similar effect is produced by chloroform. No effect is produced by toluene or thymol. Sunlight, which increases the formation of starch in algæ, does not influence the production of amylase. The action is diminished by desiccation. Optimum action in a phosphate mixture is observed at $P_H=4$—5 in the case of *Cl. glomerata*. Saccharase is increased in solutions of sucrose, dextrose, or lactose, slightly diminished by maltose and galactose, and unaffected by glycerol. Catalase is diminished in activity by pre-treatment with alcohol or by the presence of chloroform or toluene, but is increased by drying the algæ. H. W.

Photo-synthesis in Marine Algæ. I. Fixation of Carbon and Nitrogen from Inorganic Sources in Sea Water. II. Increase of Alkalinity of Sea Water as a Measure of Photo-synthesis. BENJAMIN MOORE, EDWARD WHITLEY, and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1921, **92**, [*B*], 51—60). The results confirm and amplify those reported for fresh-water algæ (A., 1920, i, 466). Marine algæ can fix elemental nitrogen from water, and thus indirectly from air, in the presence of sunlight, but not in darkness. The store of bicarbonates of calcium and magnesium present in sea water furnishes an abundant source of carbon dioxide utilisable for carbon fixation, and as fixation proceeds the sea water becomes more alkaline. The limit of alkalinity is that at which all bicarbonates have become converted into carbonates, and at this point the potential of hydrogen-ion concentration has fallen below the value $P_H=10^{-9\cdot1}$. In the strong sunshine of spring and summer this degree of alkalinity is sufficient to favour increased rapidity of cell division and induce abnormal and varying forms. J. C. D.

Photo-synthesis in the Algæ Florideæ. RENÉ WURMSER and (MME) J. DUCLAUX (*Compt. rend.*, 1920, **171**, 1231—1233).—The two species examined were *Chondrus crispus* and *Rhodymenia palmata*, the reddest and the greenest being compared, the velocity of assimilation of equal surfaces being measured by the method of Osterhout and Haas. Assimilation was most energetic in the individuals rich in phycoerythrin. Measurements of the chlorophyll and lipochrome content showed that the red specimens contained more chlorophyll than the green, but practically the same amount of lipochromes. In individuals poor in phycoerythrin the ratio chlorophyll/lipochromes was abnormally low. W. G.

New Source of Santonin. HENRY G. GREENISH and CONSTANCE E. PEARSON (*Pharm. J.*, 1921, **106**, 2—3).—The leaves of *Artemisia brevifolia*, a plant growing abundantly in Cashmir and Western Thibet at an altitude of 9000 to 14,000 feet, yield about 1% of santonin. W. P. S.

The Globulin of the Cohune Nut, *Attalea Cohune*. CARL O. JOHNS and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1920, **45**, 57—67).—The globulin from this nut resembles the globulin of the coconut. Analyses of the amino-acids present indicate that the percentages of arginine and lysine are high. Tryptophan is also present. J. C. D.

Mustard Seeds and Substitutes. I. Chinese Colza, *Brassica campestris chinoleifera*, *Viehoever*). ARNO VIEHOEVER, JOSEPH F. CLEVENGER, and CLARE OLIN EWING (*J. Agric. Research*, 1920, **20**, 117—140).—A botanical and chemical study of seeds of *Brassica campestris chinoleifera*, Viehoever, sold as mustard seed. The volatile oil obtained from these seeds was identified as crotonylthiocarbimide, which is not a suitable substitute for mustard oil, in respect to condimental, bactericidal, or medicinal value. [See, further, *J. Soc. Chem. Ind.*, 1921, Mar.] W. G.

The Latex of *Lactarius vellereus*, *Fr*. JULIUS ZELLNER (*Zeitsch. physiol. Chem.*, 1920, **111**, 293—296).—The latex of *Lactarius vellereus* consists of 80·5% of water, 14·65% of a mixture of stearic acid and a resin, with smaller amounts of mannitol, dextrose, mineral substances, and proteins. The acid and resin can be extracted from the dried latex with ether, from which the acid crystallises out on concentration, and the resin remains in the mother liquor. S. S. Z.

Chemistry of the Higher Fungi. XIV. *Lactarius rufus*, *Scopol.*, *L. pallidus*, *Pers.*, and *Polyporus hispidus*, *Fr*. JULIUS ZELLNER (*Monatsh.*, 1920, **41**, 443—453. Compare A., 1919, i, 140).—The light petroleum extract of *Lactarius rufus* consists mainly of free fatty acids, especially lactarinic acid (Bougault and Charaux, A., 1911, i, 835, 949; 1912, ii, 289); the liquid fatty acids were not investigated. The ethereal extract yields (1) in small proportion a substance which resembles ergosterol and gives the colour reactions characteristic of the phytosterols, and (2) a reddish-yellow resin; the burning taste of the fungus appears to be due, not to the resin, but to an accompanying substance volatilised or decomposed on boiling. The alcoholic extract contains mannitol, a sugar yielding phenylglucosazone, and choline (?). The aqueous extract contains viskosin, carbohydrates of the mycetide type, and the ions PO_4''' and $K^{\cdot}$ in large proportions, SO_4', Cl', and $Mg^{\cdot\cdot}$ in small proportions, and $Ca^{\cdot\cdot}$ in traces.

The light petroleum extract of *Lactarius pallidus* contains large proportions of free fatty acids, chiefly lactarinic acid, the ethereal extract, a small proportion of a substance resembling ergosterol, the alcoholic extract, much mannitol, and traces of dextrose and basic substances (choline), and the aqueous extract viskosin, mycetide, protein derivatives apparently of high molecular weight, and the inorganic constituents found in *L. rufus*. The membranous tissues yield on hydrolysis by means of acid, glucosamine, dextrose,

and traces of pentoses, but no mannose, galactose, or methylpentose.

The light petroleum extract of *Polyporus hispidus* contains mainly fatty acids; the ethereal extract, much resin (compare Zopf, A., 1889, 919), giving catechol and phloroglucinol when fused with potassium hydroxide, and, in small proportions, substances resembling ergosterol; the alcoholic extract, dextrose, choline, a phlobaphen which is apparently allied to the resin and is not of glucosidic character, and the aqueous extract, a carbohydrate of the mycetide type, and the usual inorganic constituents. The membranous matter yields, on acid hydrolysis, glucosamine, dextrose, and small proportions of pentose. T. H. P.

Microchemistry of Plants. XIV. Blueing of Plant Ash by Zinc Chloro-iodide. XV. Separation of Fat Drops on the Fruit of an Apple (*Malus coriarius*). HANS MOLISCH (*Ber. deut. bot. Ges.*, 1920, **38**, 299—306. Compare A., 1919, i, 113, 242).—XIV. When a piece of sodium carbonate the size of a poppy-seed is treated on a microscope slide with a drop of zinc chloride–iodine solution (zinc chloride, 100 grams; potassium iodide, 32·5 grams; iodine, 6·5 grams; and water, 52·5 grams), and covered with a cover-glass, microscopic examination reveals vigorous evolution of gas and formation of a filmy precipitate, which with the soda particles is coloured intensely violet to indigo-blue. Of a number of salts examined, lithium, potassium, ammonium, silver and barium carbonates, and potassium nitrite give the same reaction, but this is not obtained with any of the organic salts tried. The reaction depends on the formation of bubbles of carbon dioxide, on which is deposited basic zinc carbonate or hydrated zinc oxide, iodine being taken up by the latter, as in a solid solution, with a blue coloration.

Of the ashes of plants in which calcium oxalate occurs, only certain ones give this blue coloration; in these cases it may be that the oxalate present is a double calcium–potassium salt.

XV. The fruit of *Malus coriarius* exhibits at its surface small, clear drops of oil, which impart a greasy feel; this is the first case of such a phenomenon with a living fruit. T. H. P.

The Presence of Uricase in the Plant Organism. ANTONIN NĚMEC (*Biochem. Zeitsch.*, 1920, **112**, 286—290).—Soja-bean meal in the presence of atmospheric oxygen can degrade uric acid, with the ultimate formation of ammonia. S. S. Z.

Toxic Action of Compounds of Arsenic, Antimony, and Fluorine on Cultivated Plants. A. WÖBER (*Angew. Botanik.*, 1920, **2**, 161—178; from *Chem. Zentr.*, 1921, i, 35—36).—A general toxic dose of a given poison for phanerogams cannot be indicated, since marked differences are observed in the behaviour of different plants towards the same poison. Scarlet runners and seedling peas are most readily affected, whilst barley, oats, wheat,

maize, and rye are less sensitive. In water cultures, 0·01 gram of arsenious oxide per litre is strongly toxic, but the action of arsenic oxide is less pronounced; 0·1 gram per litre is fatal to all plants. Antimony is much less poisonous. Sodium fluoride is harmful when present to the extent of 0·1 gram per litre. When scattered on the soil, arsenious oxide is less toxic than arsenic oxide; antimonious oxide is still less poisonous (0·5 gram per 100 grams of soil is necessary), and has about the same action as sodium fluoride. In 0·1% solution, arsenic oxide is more toxic than arsenious oxide when used for spraying the green parts of plants, but with the sodiun salts the order is reversed. Corrosive action is not exhibited by sodium fluoride solutions containing less than 1% of the salt. H. W.

The Respective Rôle of the Three Bases: Potash, Lime, Magnesia, in Cultivated Plants. H. LAGATU (*Compt. rend.*, 1921, **172**, 129—131).—Taking the analyses of numerous plants, the author has calculated the basic equivalents $K_2O/2$, $CaO/2$, $MgO/2$ in 100 basic equivalents attributable to these three bases. These results are plotted on a triangular graph, the relative contents of the three bases in the various crops being indicated by points. It is seen that the ratio MgO/CaO is >1 in the case of sugar-beet, maize, potatoes, and mangels, exactly 1 in the case of wheat, and only just under 1 in oats, rye, barley, and buckwheat. W. G.

Mechanism of the Fertilising Action of Sulphur. G. NICOLAS (*Compt. rend.*, 1921, **172**, 85—87).—Experiments to see whether sulphur favoured the formation of nodule bacteria on leguminosæ gave negative results, but it seems to exercise a considerable, favourable influence on the carbon assimilation of the plant, owing to its influence on the development of chlorophyll. The optimum amount of sulphur to apply varies with the species of the plant. W. G.

Relation of the Soil Solution to the Soil Extract. D. R. HOAGLAND, J. C. MARTIN, and G. R. STEWART (*J. Agric. Res.*, 1920, **20**, 381—395).—It has previously been shown that the variations in the total solids present in an aqueous extract of soil due to season and crop growth is in fairly satisfactory agreement with the variations in the concentration of the soil solution as determined by the freezing-point method of Bouyoucos and McCool (compare Hoagland, *J. Agric. Res.*, 1918, **12**, 369). Further evidence is now given in support of this statement. It is shown that the various elements or ions present in a concentrated aqueous extract, made with 1 part of soil to ½ or 1 part of water, are apparently in the same proportion as in the soil solution. When such an extract is made and concentrated until it has exactly the same freezing-point depression as the moist soil, and the extract is again filtered

through the soil, it is found that it retains the same concentration and that the different ions are present in the same proportion. This balance is, however, considerably upset if a small amount of potassium sulphate is added to the extract before filtering it through the soil. An aqueous soil extract is composed chiefly of the solutes present in the soil solution, plus substances dissolved from "adsorbed" or easily soluble components of the soil, the latter fraction being dependent in part on the concentration and composition of the soil solution and the composition of the adsorbed material relative to the soil solution. Successive leachings of eight parts of soil with one part of water gave extracts which varied very little in their rates of individual solutes present, except possibly in so far as the nitrate ion was concerned. The authors consider that the concentration of the phosphate in soil solution is usually very low, but that immediate replacement occurs as phosphate is absorbed by the plant, thus producing a constant concentration of phosphate over long periods of time. W. G.

Effect of Season and Crop Growth on the Physical State of the Soil. D. R. Hoagland and J. C. Martin (*J. Agric. Res.*, 1920, **20**, 397—404).—Aqueous extracts of cropped and uncropped soils were prepared, using 1 part of soil and 2 parts of water. The concentration of this extract was determined by conductivity measurements, and the colloidal matter in the soil estimated approximately by turbidity measurements after the soil had been allowed to settle in the water for twenty-four hours. The results indicate that the physical state of certain soil constituents is influenced to a marked degree by the concentration of the soil solution. There is a considerable seasonal variation in the colloidal state of the soil suspension, and a large increase in colloidal matter is noted when the soil solution is depleted as a result of absorption of solutes by the plant. W. G.

Soil Reaction. I. A Résumé. E. A. Fisher (*J. Agric. Sci.*, 1921, **11**, 19—44).—The author first discusses the various theories of soil acidity put forward by different workers, and then the methods of determining soil acidity. He then considers this acidity in the light of physico-chemical conceptions of acidity, and concludes with a critical study of the Hutchinson-McLennan method of determining the lime requirement of a soil, pointing out possible sources of irregularity. W. G.

The Occurrence of Different Kinds of Carbonates in certain Soils. F. Hardy (*J. Agric. Sci.*, 1921, **11**, 1—18).—A sample of marine silt from the north-west coastal belt of the Wash was found to contain dolomite among its minerals, and, in consequence, the behaviour of this mineral was compared with that of calcium and magnesium carbonates under certain conditions. Whilst magnesium carbonate appears to retard the second stage (that is, nitrite to nitrate) of nitrification, pure dolomite appears

appreciably to retard the whole process, and ferriferous dolomite has a very marked effect. The author divides the carbonate content of a soil into "calcitoid" and "dolomitoid," the former being soluble in $N/3$-acetic acid at the ordinary temperature, and the latter insoluble in this acid. Marine silt soils may be expected to contain both forms of carbonate, but soils not directly or indirectly derived from marine silts usually do not contain dolomitoid carbonate. Cultivation for crop production reduces both the calcitoid and dolomitoid carbonate content of soils, but the former disappears much more rapidly than the latter. Soils containing both kinds of carbonate may show a "lime requirement" as determined by the Hutchinson-McLennan method (A., 1914, ii, 784), although the total carbonate content is apparently above the usual value taken as indicating deficiency of carbonate. W. G.

Occurrence of Arsenic in Soils and in Vegetable and Animal Substances, and its Forensic Importance. R. Lillig (*Pharm. Zeit.*, 1920, **65**, 500—502).—Attention is directed to the wide distribution of arsenic, the element being found in soils, vegetables, animal organs, sea-water, marine algæ, etc. The quantities present are usually very small. Arsenic has also been found in cremation ashes, particularly when the coffin had metal fittings. W. P. S.

New Method of Hydrolysing Proteins and Tissues in the Cold. Domenico Lo Monaco (*Arch. Farm. sper. Sci. aff.*, 1920, **30**, 97—102).—When subjected to the action of chlorine, bromine, or carbonyl chloride vapour, all animals except those with a coriaceous or chitinous skin undergo mummification, previous removal of the viscera being unnecessary. Treatment in the cold with chlorine or bromine vapour produces hydrolysis of proteins and other changes capable of wide application. Thus, fresh foods, such as fish, game, seeds, etc., may be made to retain their fresh appearance and odour, the treated materials causing no ill-effects when eaten. After such treatment, fresh peas and beans germinate readily, giving, out of season, robust plants bearing flowers and fruit. Further, dried seeds exhibit increased growth after the treatment, and a similar result is obtained when hyacinths are grown in dilute chlorine water. Analogous effects are obtained when seeds are sown in soil mixed with vegetable matter previously treated with bromine or chlorine; the inorganic constituents of the soil are also rendered soluble to a large extent by this treatment. Leather and cloth cuttings are rapidly reduced to a dense, soluble, pasty mass by the halogen vapour. T. H. P.

Organic Chemistry.

Water Gas. Léo Vignon (*Ann. Chim.*, 1921, **15**, 42—60).—Using carbon very poor in mineral matter, and in particular poor in lime, the proportion of methane in the water gas diminishes. The origin of methane in water gas is shown by the three reactions:

$$4CO + 2H_2O = 3CO_2 + CH_4.$$
$$2CO + 2H_2 = CO_2 + CH_4$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$

Below 800°, the formation of calcium carbonate is an important factor in the production of methane. Above 900°, the carbonate is decomposed and the calcium oxide acts catalytically, favouring the above three reactions. It is possible, by the action of calcium oxide, to convert carbon monoxide into a mixture of hydrogen and hydrocarbons. Other substances may act as catalysts, favouring the interaction of carbon monoxide and water vapour to give methane. With certain catalysts, such as iron, alumina, or silica, there is probably an intermediate formation of a carbide, which is decomposed by the water vapour. In other cases hydrogen may be formed and this will then react with the carbon monoxide or dioxide to give methane. (See, further, *J. Soc. Chem. Ind.*, 1921, 206A). W. G.

Preparation of Isoprene from Light Camphor Oil. Yûshichi Nishizawa (*J. Tokyo Chem. Soc.*, 1920, **41**, 1048—1054).—Isoprene was prepared by passing light camphor oil through a glass tube containing a catalyst and heated at 500°. The following catalysts were used; the numbers in the bracket show the percentage yield of isoprene and of the fraction of b. p. 105—110°: (*a*) Asbestos covered with soot (2, –). (*b*) Asbestos coated with reduced silver (8, 7). (*c*) Copper wire gauze electrically plated with silver (6, 9). (*d*) Pumice with reduced silver (6, 8). (*e*) Powdered pumice (10, 9). K. K.

Preparation of Methyl Bromide. Georg Schroeter (D.R.P., 330642; from *Chem. Zentr.*, 1921, ii, 447).—Bromine is mixed with methane or gaseous mixtures containing methane and led over catalysts, particularly iron, at temperatures above 200°. Methane is passed through liquid bromine and subsequently over iron powder heated at 250—300°; with tubes of 20 mm. diameter, heated over a length of 250 mm., the mixture can be passed at a rate of more than 3 litres per minute without allowing bromine to escape reaction. At a rate of 2 litres per minute and with a column of bromine 5—6 cm. in height, a gaseous mixture containing 50% of unchanged methane is obtained. Methylene bromide and bromoform are also produced from mixtures containing a greater proportion of bromine. The iron may be replaced by

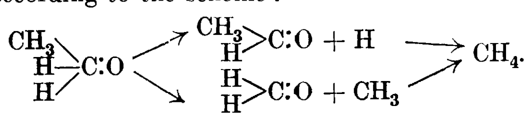
copper, nickel, cobalt, mixtures of these metals and their compounds, or by other metals which can occur in different states of valency. H. W.

Halogen Derivatives of Nitroform. ALEXANDER KILLEN MACBETH and DAVID DOIG PRATT (T., 1921, **119**, 354—358).

Rearrangement of Nitroparaffins. E. BAMBERGER (*J. pr. Chem.*, 1920, [ii], **101**, 328—332).—Nitrosoethyl alcohol is produced on acidification of an alkaline solution of nitroethane (Bamberger and Rüst, A., 1902, i, 197) as an intermediary between ethylidenenitronic acid and acethydroxamic acid (Steinkopf and Jürgens, A., 1912, i, 152; compare Bamberger and Scheutz, A., 1901, i, 587). But it is not observed in the oxidation of amines and oximes to nitronic and hydroxamic acids (A., 1900, i, 508; 1903, i, 83, 84, 152), and it therefore appears that in this case these products are produced independently of each other, like the benzenediazoic acids and nitrosoarylhydroxylamines from the oxidation of diazoxides (A., 1909, i, 907; 1912, i, 733). The same applies to the oxidation of β-naphthylnitroamine by potassium ferricyanide, which gives rise to β-diazoic acid and β-naphthaquinone-β-diazide. The latter cannot be generated from the former in neutral or weakly alkaline solution, although this is possible with the corresponding *a*-derivatives. J. K.

The Dehydrogenation of Alcohols by Catalytic Oxidation. CHARLES MOUREU and GEORGES MIGNONAC (*Bull. Soc. chim.*, 1921, [iv], **29**, 88—101).—A full account of work already published (A., 1920, i, 283, 805). W. G.

The Electrolytic Oxidation of Methyl and Ethyl Alcohols in Alkaline Solution. The Electrolytic Formation of Methane. ERICH MÜLLER and ANTONIO RIUS Y MIRÓ (*Zeitsch. Elektrochem.*, 1921, **27**, 54—57).—By the electrolytic oxidation of methyl alcohol in aqueous sodium hydroxide at the ordinary temperature at a platinum anode, small quantities of hydrogen are formed, but at most only about 11% of the theoretical, calculated on the hydrogen liberated at the cathode. Under similar conditions, ethyl alcohol gives a mixture of hydrogen and methane, also in small yield. To account for the phenomena, the hypothesis is put forward that the alcohol, *e.g.*, methyl alcohol, is first ionised, and that the ion $H_3C{\cdot}O'$ is oxidised into an oxy-alcohol, $H_3C{:}O$, which breaks down, according to the equation $H_3C{:}O \rightarrow CH_2O + \frac{1}{2}H_2$, into aldehyde and hydrogen. In the case of ethyl alcohol, the oxy-alcohol, $CH_3{\cdot}CH_2{:}O$, may break down into acetaldehyde and hydrogen, or it may form methane according to the scheme:



The formation of ethane should be possible under this scheme, but at most traces of it appear. The formation of ethane and carbon

dioxide by the electrolysis of acetates can be explained on similar lines. E. H. R.

The Preparation of Rhamnose. C. F. Walton, Jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 127—131).—The commercial product "Lemon Flavin" is rich in quercitrin and forms an excellent starting material for the preparation of rhamnose. The material is subjected to direct acid hydrolysis, and a 20—25% yield of rhamnose can be obtained. (See, further, *J. Soc. Chem. Ind.*, 1921, April). W. G.

Solubility of Ethyl Ether in Solutions of Sodium Chloride. Percy Cyril Lesley Thorne (T., 1921, **119**, 262—268).

Esterification by Zirconium Oxide. A. Mailhe and F. de Godon (*Bull. Soc. chem.*, 1921, [iv], **29**, 101—106).—Zirconium oxide acts as a good catalyst in the preparation of esters of aliphatic acids by passing the mixed vapours of the acid and alcohol over the oxide at 270—290°. The yield of ester depends on the weight of oxide used, the velocity of flow of the vapours, and the proportion of alcohol and acid used. W. G.

A New Hydroxystearic Acid from "Hardened" Castor Oil. H. Thoms and W. Deckert (*Ber. deut. Pharm. Ges.*, 1921, **34**, 20—26).—By crystallisation of a "hardened" castor oil (m. p. 80°, iodine value 12) from alcohol a glyceride was isolated which on saponification gave λ-*hydroxystearic acid*, m. p. 83°. For characterisation there were prepared the *ethyl* ester, needles, m. p. 44°; the *anilide*, m. p. 119°, and the o-*toluidide*, m. p. 123°. By oxidation with chromic acid λ-*ketostearic acid* was formed, which crystallised from acetic acid in large rhombic leaflets, m. p. 82°, and gave an *ethyl* ester, m. p. 38°, and a *semicarbazone*, prisms, m. p. 125°. The position of the hydroxyl group in the hydroxystearic acid was determined by dehydrating the acid with boiling 60% sulphuric acid to a mixture of *iso*oleic acids which could not be separated. These were then oxidised with alkaline permanganate, and the mixture of acids produced was esterified, and subjected to repeated fractional distillation in a vacuum, whereby the ethyl esters of hexoic, heptoic, and decane-ακ-dicarboxylic acids were isolated and identified, thus showing that the *iso*oleic acids were the Δ^{κ}- and Δ^{λ}- isomerides, and that the original hydroxyl group must have occupied the λ-position. It further follows that in the hydrogenation of the castor oil no displacement of the hydroxyl group of the ricinoleic acid occurs. G. F. M.

The Reaction of Sodium Salts with Uranyl Acetate alone and in the Presence of Salts of Magnesium, Zinc, Cadmium, and Glucinum. Stanko S. Miholić (*Bul. Acad. Sci. Zagreb.*, 1920, 16—23).—Sodium uranyl diacetate has a solubility of 4·62 grams in 100 grams of solution at 20°. Sodium uranyl magnesium triacetate crystallises with $6H_2O$ and sodium uranyl zinc triacetate with $4\frac{1}{2}H_2O$. None of these salts can be used for the estimation

of sodium owing to the solubility of the diacetate and the tendency of the triacetate to vary in composition according to the conditions under which it separates. The author was not able to obtain triacetates containing cadmium or glucinum. W. G.

A New Calcium Salt. LOUIS GAUCHER and GEORGES ROLLIN (*Compt. rend.*, 1921, **172**, 390).—When lactic acid in concentrated solution is treated with phosphorus iodide, a *compound*, $C_6H_9O_6P$, m. p. 120°, which is apparently an anhydride, is obtained. Treated with water, it yields *di-α-carboxyethyl hydrogen phosphite*, $HO\cdot P(O\cdot CHMe\cdot CO_2H)_2$, which, when exactly neutralised by calcium hydroxide, gives a *calcium* salt, $Ca_3(C_6H_8O_7P)_2,8H_2O$. The acid is thus tribasic. This calcium salt is quite stable in cold, neutral aqueous solutions, but is readily decomposed by alkalis, giving calcium phosphite. W. G.

Odorous Constituents of Apples. Esters derived from Leucic Acid. SHINTARÔ KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 965—975).—Power and Chesnut (A., 1920, i, 653) have proved that amyl esters of formic, acetic, and hexoic acids are the principal odorous constituents of apples. As in Japan the hydrolysis of proteins is carried out on a manufacturing scale, efforts have been made to obtain the odorous constituents of fruits or flowers and analogous esters from the by-products of the decomposition. The following esters were prepared, most of which have a fragrant odour: *ethyl α-acetoxy*iso*hexoate*, b. p. 120—121°/20 mm., the corresponding *methyl* ester, b. p. 99—100°/20 mm.; *ethyl α-benzoyloxy*iso*hexoate*, b. p. 174—176°/17 mm.; ethyl α-*iso*valeryl*iso*hexoate, b. p. 125—128°/10 mm.; *ethyl α-chloro*iso*hexoate*, m. p. 152—153°/10 mm., the *amyl* ester, b. p. 113—114°/8–10 mm., these can be converted into the corresponding esters of *iso*hexoic acid by reduction with sodium amalgam. α-Acetoxy*iso*hexoic acid phenyliminochloride forms prisms, which when treated with acetic ester and magnesium yield *α-ethoxy*iso*hexaldehyde* as an oil. K. K.

Elucidation of the Constitution of Glycerides. AD GRÜN and FRANZ WITTKA (*Ber.*, 1921, **54**, [*B*], 273—289).—The uncertainty with regard to the constitution of synthetic glycerides to which attention has been directed recently by Fischer, Bergmann, and Bärwind (A., 1920, i, 845) and previously by Abderhalden and Eichwald (A., 1916, i, 8) has been also observed by the authors, who have been drawn to the conclusion that it extends, not merely to those cases in which an intermediate glycide formation is possible, but also, as a consequence of the extreme ease with which alkyl interchange occurs with glyceryl esters, to the majority of other synthetic glycerides. The present communication contains an account of attempts to elucidate the constitution of di- and monoglycerides by a study of the products of their oxidation. αβ-Diglycerides would be expected to pass into the corresponding aldehydes and then into diacylglyceric acids, whilst αγ-diglycerides should yield derivatives of dihydroxyacetone. This expectation is fulfilled to a certain extent, and although the keto-derivatives

have not been isolated in substance, their presence can be proved by Strache's method for the estimation of the ketonic group (treatment with an excess of phenylhydrazine and estimation of the amount of the latter unused by oxidation with Fehling's solution and measurement of the nitrogen evolved). The monoglycerides can theoretically give rise to a much greater number of products; the α-derivatives yield acyloxypyruvic acids and ultimately acylglycollic acids, whilst the β-isomerides give acyltartronic acid. Unfortunately, the latter substance is unstable under the experimental conditions adopted and breaks down into acylglycollic acid, thus making the method useless for distinguishing between α- and β-monoglycerides, for which, however, the acetone method of Fischer and his co-workers is eminently suitable.

The synthetic distearin obtained from $\alpha\gamma$-dichlorohydrin and potassium acetate, m. p. 74·5° (after preservation), was suspended in glacial acetic acid and oxidised at 35° with finely divided potassium permanganate, which was added gradually; the product consisted of unchanged material and a fraction containing about 20% of ketone (aldehyde is shown to be absent by the usual qualitative reactions). The preparation therefore consisted of $\alpha\gamma$-distearin mixed with a small quantity of the $\alpha\beta$-isomeride. A synthetic distearin, m. p. 77·5°, prepared from α-monochlorohydrin and stearyl chloride and subsequent treatment of the product with silver nitrite, is shown to be a mixture of approximately equal amounts of $\alpha\gamma$- and $\alpha\beta$-distearin, since, when oxidised, it yielded unchanged material, a small amount of acidic products which were not definitely identified (probably glyceric acid derivatives), distearoxyacetone, and the distearyl ester of distearylglyceric acid, $C_2H_3(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}CO{\cdot}O{\cdot}C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2$.

The products obtained by the stepwise hydrolysis of tristearin with sulphuric acid (compare Grün and Corelli, A., 1912, i, 409) have been further investigated; improvements in the process are introduced by mixing the glyceride with sulphuric acid (100%, 3·2 molecular proportions) heating the mixture at 70°, and immediately adding it to boiling sodium sulphate solution (2%) which is subsequently treated with sodium chloride. In this manner a mixture of monostearin (2·3%), distearin (79·7%), and tristearin (18·0%) is ultimately obtained, but the analytical data of the crude product indicate a considerably greater percentage of monostearin, so that it appears that the greater part of the latter suffers hydrolysis probably during the neutralisation of the crude product. It is noticeable that, in one instance, an apparently pure distearin, leaflets, m. p. 56°, was isolated, which is probably the modification of lower melting point of a distearin; after being kept for a year, the melting point rose to 66°. Oxidation of the distearin of higher melting point (77·5°) gave a mixture of unchanged substance, distearoxyacetone and distearin distearylglyceric ester (the latter appears to exist in two modifications, the one having m. p. 68°, the other melting with the heat of the hand). Similar treatment of the distearin of lower melting point gave acidic products of indefinite character and neutral substances containing considerable

quantities of distearoxyacetone and only very small quantities of ester, thus showing that $\alpha\gamma$-distearin is actually present in the mixture.

Oxidation of monostearin obtained by hydrolysis of tristearin with sulphuric acid or by the step-wise alcoholysis of the latter gave a mixture of unchanged material and *stearyloxyacetic acid*, shining aggregates of colourless needles, m. p. 80°. The latter acid was also prepared by the interaction of potassium stearate and potassium chloroacetate in alcoholic solution; it is remarkable that the unused stearic acid combines with the ester acid to form a very stable additive compound, $C_{38}H_{74}O_6$, colourless, shining leaflets, m. p. 76°.

Monostearin, obtained from α-monochlorohydrin and potassium stearate, is almost quantitatively transformed by phenylcarbimide at 115° into the corresponding *diphenylurethane*, m. p. 86°; the monostearin derived from tristearin by alcoholysis or by the action of sulphuric acid, however, gave only a small yield of a diphenylurethane, m. p. 89°, the main product being diphenylcarbamide, mere traces of which are formed with the first compound; at present, these results appear very difficult to interpret. H. W.

Alkyl Interchange and its Relationship to the Constitution of Fats. AD. GRÜN [with FRANZ WITTKA and JOSEF SCHOLZE] (*Ber.*, 1921, **54**, [*B*], 290—299).—Renewed attention has recently been directed by Fischer (A., 1920, i, 808) to the ease with which interchange of alkyl groups occurs between fats and alcohols in the presence of suitable catalysts. It is now shown that the phenomenon is also observed in the absence of catalysts, although under somewhat more drastic conditions. The anomalies in the melting points of diglycerides and mixed triglycerides have been explained as a consequence of alkyl interchange occurring slowly and at the ordinary temperature in the absence of catalysts, but this hypothesis is insufficient to cover all the facts, since tristearin exists in two forms, m. p. 55° and 71° respectively, whilst trilaurin can occur in a permanently liquid form. The author prefers to regard these as examples of co-ordination isomerism (compare *Öl and Fett. Ind.*, 1919, **1**, 225, 252), in which every ester may be regarded as an equilibrium mixture of the forms $R\cdot C\Big<{}^{O}_{OR'}$ and $R\cdot C\Big<{}^{O}_{O}\Big\}R_1$. A monoglyceride can therefore exist in the two isomerides, $(OH)_2C_3H_5\cdot O\cdot C\Big<{}^{O}_{R}$ and $(OH)_2C_3H_5 \,\vdots\vdots\vdots\, O_2CR$, a diglyceride as

$$HO\cdot C_3H_5\left(O\cdot C\Big<{}^{O}_{R}\right)_2,\quad HO\cdot C_3H_5\begin{array}{l}\cdot\cdot\,{}^{O}_{O}\!>CR\\ \diagdown O{-}C\Big<{}^{O}_{R}\end{array}\ \text{and}\ HO\cdot C_3H_5\begin{array}{l}\cdot\cdot\,{}^{O}_{O}\!>CR\\ \cdot\cdot\,{}^{O}_{O}\!>CR\end{array}$$

whilst a triglyceride formed from a single acid can exist in four forms, the pure ester and pure co-ordination varieties and two mixed types. The co-ordination form of a triglyceride formed from a single acid can naturally only pass into the true ester form, but from the similar form of a mixed triglyceride, a mono- or

diglyceride, all the structural isomerides can in addition be produced.

The reaction between tristearin and ethyl and *iso*amyl alcohols respectively is best effected by heating equal weights of the components in an autoclave at 200° and 270° respectively during known intervals of time. The bulk of the unused alcohol is removed by distillation, the residue melted with water to eliminate alcohol and glycerol, and the amount of ethyl or *iso*amyl stearate estimated by fractionation of the residue under diminished pressure, whereby the former passes over at 175—180°/3 mm. and the latter at 186—190°/2 mm. The method is accurate to within about 1%. Unfortunately, the results are not strictly comparable among themselves, since reaction occurs, in part, at any rate, in a heterogeneous system, for which efficient mixing could not be provided. It is shown, however, that a definite equilibrium is ultimately attained in each case and that ethyl and *iso*amyl stearates are produced in considerable amount; the tristearin is partly unchanged and partly converted into di- and mono-stearin. Only a portion of the liberated glycerol could be recovered, the remainder having suffered decomposition.

The action of ethyl and *iso*amyl stearates with glycerol in varying proportions has been examined by treating the thoroughly agitated components in an open flask for definite periods at 270—280°; under these conditions the liberated alcohol is volatilised and the action ultimately proceeds to completion. Analytical investigation of the glycerides formed after definite intervals points to a very complicated course of the reaction. Apparently, ester and glycerol yield primarily monostearin which dissolves the excess of ester and reacts further, with production of distearin; the latter is likewise soluble in the ester and, if a sufficient excess of glycerol is not present, can then form tristearin. If, however, glycerol is present in excess, the back action occurs, with production of monostearin. H. W.

The Conditions Underlying the Formation of Unsaturated and of Cyclic Compounds from Halogenated Open-chain Derivatives. I. Products derived from α-Halogenated Glutaric Acids. CHRISTOPHER KELK INGOLD (T., 1921, **119**, 305—329).

The Mechanism Underlying the Reaction between Ethyl Cyanoacetate and Tautomeric Substances of the Keto-enol Type. CHRISTOPHER KELK INGOLD (T., 1921, **119**, 329—341).

Synthesis of the Polyacetic Acids of Methane. I. The Conditions Controlling Synthesis by the Cyanoacetic Ester Method, and the Preparation of Methanetriacetic Acid. CHRISTOPHER KELK INGOLD (T., 1921, **119**, 341—354).

α-Sulphodipropionic Acid. J. M. LOVÉN and R. AHLBERG (*Ber.*, 1921, **54**, [*B*], 227—229).—Optically inactive α-sulphodipropionic acid, $SO_2(CHMe{\cdot}CO_2H)_2$, m. p. 170—172°, is obtained when

d-, *l*-, *r*-, or *meso*-α-thiodipropionic acid, $S(CHMe{\cdot}CO_2H)_2$, is oxidised by permanganate in neutral solution and in the presence of carbon dioxide to neutralise the alkalinity otherwise developed; the identity of the products is confirmed by estimation of their specific conductivity. Attempts to resolve *r*- and *meso*-α-thiodipropionic acid by means of the optically active α-phenylethylamines are also described, which, however, were unsuccessful; in each case, a well-crystallised normal *salt* was obtained, but the hydrogen salts could not be prepared in the crystalline condition. H. W.

Action of Ammonia on Acetone. THOMAS STEWART PATTERSON and ANDREW MCMILLAN (T., 1921, **119**, 269—271).

Optically Active Cobalt Salts with β-Diketone Residues in the Complex. A. WERNER, JEANNE E. SCHWYZER, and WALTER KARRER (*Helv. Chim. Acta*, 1921, **4**, 113—129).—The view that metallic salts of the diketones are to be regarded as internal complex salts in which a β-diketone residue occupies two co-ordination positions at the central atom (A., 1901, i, 682) was rendered probable by the observation that the simplest β-diketone, namely, acetylacetone, may be readily introduced into a cobalti-complex in place of two co-ordinative univalent groups (Werner and Matissen, A., 1918, i, 379). That this view is correct is now shown by the preparation of the acetylacetonatodiethylenediaminecobalt salts:

$$\left[CH{<}\begin{matrix} CMe{\cdot}O \\ CMe{:}O \end{matrix}{>}Co\,en_2 \right]X_2,$$

and the corresponding propionylacetonato-salts in two optically active forms. If an optically active 1 : 2-chloro-aquodiethylenediamine cobalt salt is treated with the calculated amount of aqueous potassium hydroxide and the resulting hydroxo-aquodiethylenediaminecobalt salt, without isolation from the solution, is gently heated with rather more than the calculated proportion of the β-diketone, the optically active acetyl- or propionyl-acetonato-compounds are obtained. Racemisation occurs, especially with the latter compounds, but the iodides are readily decomposed into the pure optically active fractions by crystallisation from alcohol.

The optically active chloro-aquo-compounds required are obtained by resolving the racemic compounds by means of *d*-α-bromocamphor-π-sulphonic acid.

The new compounds, which in their external properties closely resemble the acetylacetonatodiethylenediaminecobalt salts already described, form garnet-red crystals, minium-red powders, and bright blood-red solutions. The β-diketone residues are very stably held, and the salts may be crystallised or their solutions evaporated to dryness without decomposition. The salts exhibit high rotations of the same sign as those of the corresponding active chloro-aquo-salts and pronounced abnormal rotatory dispersion with a maximum at 554 $\mu\mu$. The rotations of the freshly prepared propionylacetonato-compounds are about 10% higher than those of the corresponding acetonylacetonato-compounds, and they diminish by about 15% after the lapse of four months.

l-1 : 2-*Chloro-aquodiethylenediaminecobalt bromide*,

$$1:2\left[\begin{matrix}Cl\\OH_2\end{matrix}Co\,en_2\right]Br_2,$$

and the corresponding *d*-*isomeride*, form dark violet-red prisms ($+H_2O$), $[\alpha]_D$ − or + 214°.

d- or *l*-*Acetonylacetonatodiethylenediaminecobalt iodide*,

$$[C_5H_7O_2Co\,en_2]I_2 + H_2O,$$

forms slender, garnet-red prisms, $[\alpha]_D$ + or − 400°; the *chlorides* ($+H_2O$), bright red needles, $[\alpha]_D$ + 543°, − 550°; the *bromides* ($+H_2O$), slender, shining, red or garnet-red, acicular prisms, $[\alpha]_D$ + or − 460°; the *thiocyanates* ($+2H_2O$), small, bright red crystals, $[\alpha]_D$ + or − 533°; the *perchlorates*, garnet-red prisms, $[\alpha]_D$ + or − 543°; the *persulphates*, garnet-red crystals, $[\alpha]_D$ + 433° or − 480°; and the *nitrates*, red needles, $[\alpha]_D$ + or − 550°.

r-*Propionylacetonatodiethylenediaminecobalt iodide*,

$$[C_6H_9O_2\,Co\,en_2]I_2 + H_2O,$$

forms garnet-red prisms; the *bromide* ($+H_2O$), *chloride* ($+H_2O$) and *nitrate* ($+H_2O$), garnet-red crystals; the *sulphate*, long, red needles; the *thiocyanate* and *perchlorate*, garnet-red crystals, and the *persulphate*, small, orange-red needles.

d- or *l*-*Propionylacetonatodiethylenediaminecobalt iodide* ($+H_2O$) forms garnet-red columns, $[\alpha]_D$ + 465° or − 434°; the *nitrates*, crystals, $[\alpha]_D$ + 596° or − 511°; the *perchlorates*, garnet-red crystals, $[\alpha]_D$ + 434° or − 458°, and the *persulphates*, orange-red needles, $[\alpha]_D$ + 477° or − 492°. T. H. P.

Synthesis of Inositol Hexaphosphate. S. POSTERNAK (*Helv. Chim. Acta*, 1921, **4**, 150—165).—The results previously obtained (A., 1919, i, 433) are confirmed, and Anderson's criticisms on the author's work (A., 1920, i, 663) refuted. Owing to the energetic retention, by inositol hexaphosphate and by most of its salts, of three molecules of water which it is impossible to expel, even partly, without decomposing the compounds, the author proposes to express the formula in the form, $C_6H_{18}O_{24}P_6,3H_2O$. T. H. P.

The Existence of Hydrated or Anhydrous Compounds of Sucrose with certain Salts. W. D. HELDERMAN (*Arch. Suckerind Med. Indie.*, 1920, 1701—1714; from *Chem. Zentr.*, 1921, i, 277—278).—The solubility and cooling curves of the following systems have been investigated: sucrose, K_2SO_4,H_2O; sucrose, KCl,H_2O; sucrose, $NaCl,H_2O$; sucrose, $KC_2H_3O_2,H_2O$; sucrose, potassium oxalate, H_2O. Evidence of the formation of a chemical compound was not obtained in any instance (contrast Peligot, *Ann. Pharm.*, 1839, **30**, 71). H. W.

The Chemistry of the Polysaccharides. M. SAMEC (*Biochem. Zeitsch.*, 1921, **113**, 255—256).—Polemical. Herzfeld's and Klinger's views on the polysaccharides (A., 1920, i, 713) are criticised. S. S. Z.

Plant Colloids. IX. Various Starches. M. SAMEC and H. HAERDTL (*Koll. Chem. Beihefte*, 1920, **12**, 281—300. Compare A., 1919, i, 472).—The appearance, viscosity, osmotic pressure, reaction with iodine, molecular weight, electrical conductivity, phosphorus content, and the dialysable fraction of the undermentioned varieties of starch have been compared at 25° in 1% or 2% solutions: potato, wheat, rice, maize, horse-chestnut, *Marantha arund.*, *Mannihot ut.*, *Curcuma zed.*, *Oryza glutinosa*, and meadow saffron (*Colchicum autumnale*) starch. It is shown that all varieties of starch consist of an electro-dialysable fraction which is precipitable, highly viscous, and conducts an electric current (Meyer's β-amylose, Maquenne's amylopectin) and an electrodialysable fraction which is non-precipitable, non-viscous, and non-conducting (Maquenne's amylose). The relative quantities of these constituents vary from starch to starch, and dependent on this the water content of the starch grains varies, and also the viscosity of the solutions and the resistance to diastase. All starches contain phosphorus, but in different quantities. The following quantities in grams P_2O_5 are found in 100 grams of starch: potato, 0·112; meadow saffron, 0·016; Marantha, 0·031; Mannihot, 0·012; Curcuma, 0·162; horse-chestnut, 0·016; wheat, 0·105; maize, 0·034; and rice, 0·039. With changing phosphorus content the electrical conductivity changes, although in some cases the form in which the phosphorus is present appears to be different. The degree of dispersity varies with the various starches, as also does the mean molecular weight. The following values of the mean molecular weight are recorded: potato, 111,000; meadow saffron, 231,000; Marantha, 260,000; Mannihot, 208,000; Curcuma, 158,000; horse-chestnut, 230,000; wheat, 170,000; *Oryza glutinosa*, 173,000; maize, 77,500; and rice, 110,000. All starches react with alkalis, but the viscosity of the solutions is differently affected in the different cases by this action. All starch solutions lose to a greater or less extent their high viscosity when the temperature is raised, but the velocity and the extent of the fall in the viscosity are different. The molecular weight also changes with change of temperature, but differently for different varieties, thus: potato, 120°, 123,000; 138°, 111,000; 155°, 144,000; rice, 120°, 109,000; 138°, 110,000; 155°, 57,000. J. F. S.

Vegetable Glues. ERNST STERN (*J. pr. Chem.*, 1920, [ii], **101**, 308–327).—The assumption of the formation of a definite compound in mixtures of starch and aqueous alkali hydroxide (Vieweg, A., 1907, i, 893; 1908, i, 857; Pfeiffer and Tollens, A., 1882, 490) does not suffice completely to explain the phenomena, since no definite end-point to the equilibrium is attained; the progressive variations in physical properties of such mixtures leads to the conclusion that coagulation, hydrolysis, and molecular degradation to smaller complexes occur simultaneously. On the other hand, it is incorrect to assume, with Fouard (*L'état colloidal l'amidon et sa constitution physico-chimique*, Paris, 1911), that compound-formation does not occur; the reaction is on the border-line between

adsorption and chemical reaction. The conductivity of sodium hydroxide is diminished by the addition of starch, owing rather to the formation of adsorption compounds than to any mechanical effect, and variations on keeping are only observed at higher temperatures (75°), accompanied, however, by profound modification of the starch molecule. Curves are given showing that the viscosity of such solutions does vary consequent on coagulation and degradation. Similar curves in the case of starch-xanthate do not suggest the occurrence of degradation, a conclusion confirmed by the fact that starch viscose, in contrast with starch-alkali, does not deteriorate in efficiency as a glue. The conductivity of starch-xanthate is markedly less than that of starch-alkali, but gradually increases, owing, probably, to partial breaking down of the original badly-conducting complexes by separation of intact starch molecules. Colloidal solutions of the respective hydrosols, but no precipitates, are produced on the addition of metallic salts to starch-xanthate. The protective action of such solutions indicates that they contain definite compounds, since starch itself has a very slight action in this respect. Cellulose-viscose has a much smaller protective action. For technical details of the efficiency of starch-xanthate as a substitute for bone-glue see [*J. Soc. Chem. Ind.*, 1921, 234A]. J. K.

The Preparation and Fractionation of Humic Acid. V. A. BECKLEY (*J. Agric. Sci.*, 1921, **11**, 66—68).—The soil, or any other source of humus, is extracted with 4% aqueous ammonium hydroxide containing 2% of ammonium chloride. The extract is filtered on a collodion filter, any organic matter not dissolving being classed as insoluble humin. The filtrate is acidified and humus is precipitated, Mulder's *apo*crenic acid remaining in solution. The precipitate is allowed to dry and is then extracted with alcohol, which dissolves out Hoppe-Seyler's hymatomelanic acid. The portion insoluble in alcohol is called humic acid, and this is further fractionated by extraction with pyridine, a portion being soluble and the remainder insoluble in this solvent. W. G.

The Formation of Humus. V. A. BECKLEY (*J. Agric. Sci.*, 1921, **11**, 69—77).—The formation of humus both *in vitro* and in the soil proceeds in two stages. Carbohydrates react with acids, either mineral or amino-acids, to give hydroxymethylfurfuraldehyde and this then condenses to form humus. In addition, under laboratory conditions, some furfuraldehyde and lævulic acid is also produced. No evidence could be obtained of the formation of hydroxymethylfurfuraldehyde during the decomposition of cellulose by *Spirochæta cytophaga*, an organism found growing in large numbers on rotted straw. W. G.

Action of the Grignard Reagent on certain Nitric Esters. HARRY HEPWORTH (T., 1921, **119**, 251—260).

Preparation of Amino-alcohols and Cholines from Natural Amino-acids. P. KARRER, W. KARRER, H. THOMANN, E. HORLACHER and W. MÄDER (*Helv. Chim. Acta*, 1921, **4**, 76—99).—It has been stated by Gault (A., 1907, i, 752) that amino-acids with primary amino-groups, including glycine, are incapable of reduction *in vitro* to the amino-alcohols. The authors find, however, that natural amino-acids, such as alanine, leucine, phenylalanine, etc., may be reduced readily and with good yields to the corresponding amino-alcohols. The reduction takes place if the esters of the amino-acids are reduced, according to Bouveault and Blanc's method, by sodium and alcohol, but the yields are poor. Far better results are obtained by using the acetyl derivatives of the esters. If optically active amino-acids are employed, the amino-alcohols formed may also be active, although marked racemisation may occur during the reaction. Most of the amino-alcohols thus obtained are now described for the first time.

By methylation, these amino-alcohols may be converted into the corresponding cholines, but the reaction does not proceed very smoothly. The cholines have therefore been prepared by reducing dimethylaminocarboxylic esters and treating the dimethylamino-alcohols thus formed with methyl chloride or iodide: $CHMe_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CO_2Et \rightarrow CHMe_2{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CH_2{\cdot}OH \rightarrow CHMe_2{\cdot}CH_2{\cdot}CH(NMe_3Cl){\cdot}CH_2{\cdot}OH$. This method gives access to a large group of synthetic cholines intimately related to the natural amino-acids of the proteins. Leucine-choline and phenylalanine-choline, thus prepared, agree very closely in their precipitation reactions with ordinary choline, but may be distinguished by analysis of the aurichloride or platinichloride, by crystallographic examination of the platinichloride, or by the melting point of the aurichloride. The *aurichlorides* have the following properties: choline, m. p. according to various authors, 243—244°, 250—252°, 257°, 267—270°; *phenylalanine-choline*, feathery, lanceolated, yellow, crystalline aggregates, having the appearance of normally-crossed penetration twins, m. p. 114·5°; *leucine-choline* sometimes forms aggregates similar to those of the preceding compound although larger and obliquely crossed, but more often glistening, scoop-like plates and small cubes, m. p. 98—100°. The *platinichlorides* have the following properties: choline, long, yellow, rhombic needles, changing to hexagonal plates or prisms with superposed pyramids; the crystals are pseudo-hexagonal of the monoclinic system, m. p. 213—216°. *Leucine-choline*, either needles, partly united to tree-like aggregates, or flat, rhombohedral leaflets, m. p. 211—213°; the crystals are of pseudo-hexagonal habit, but belong to the rhombic system. Phenylalanine-choline, hexagonal plates or prisms with superposed pyramids, m. p. 217°; the crystals are of pseudo-hexagonal habit and probably monoclinic, but with close approximation to rhombic symmetry. With iodine and potassium iodide all three yield periodides, which from concentrated solutions separate as oils, rapidly becoming crystalline, and from dilute solutions as black crystals often exhibiting green surface lustre. When evaporated with alloxan in water, each of

the three cholines gives a red residue which is turned bluish-violet by alkali.

(Wünsche and Ritz: Like choline, leucine-choline contracts the uterus slightly, the action being greatly intensified by acetylation. Phenylalanine-choline itself exhibits this effect in marked degree.)

Not only the esters, but also the amides, of the carboxylic acids are readily reduced to alcohols, and it is probable that such reduction takes place during the putrefaction of protein, and is partly accountable for the choline observed in putrefying meat. Various proteins have been hydrolysed, the hydrolysate esterified, and the mixture of esters acetylated and then reduced by means of sodium and alcohol, the resulting mixture of amino-alcohols being fractionally distilled; the physiological effects of the products thus obtained are to be investigated later.

The new amino-alcohols which have been prepared are closely allied to the so-called proteinogenous amines, for instance, leucine alcohol to *iso*amylamine and phenylalanine alcohol to phenylethylamine. Some of these amines are employed in gynecology, since they increase the blood-pressure and contract the uterus, these effects requiring the presence of an amino-group in the β-position to the cyclic nucleus. In the amino-alcohols now obtained, the amino-group occupies the same position as in the proteinogenous amines, and it remains to be seen whether these alcohols will exert similar effects.

l-*Leucinol* (*β-amino*iso*hexyl alcohol*), $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot OH$, obtained by reducing acetyl-*l*-leucine ethyl ester by means of alcohol and sodium, is an oily liquid, b. p. 194—200°, D 0·897, $[\alpha]_D$ — 1·94°, with an aminic odour, and is probably largely racemised. The *hydrochloride*, $C_6H_{15}ON,HCl$, forms glistening, white crystals, m. p. 148—150°, and is slightly lævorotatory. With carbon disulphide and powdered potassium hydroxide, *l*-leucinol gives the *potassium* salt of a *substituted dithiocarbamic acid*, $CHMe_2\cdot CH_2\cdot CH(CH_2\cdot OH)\cdot NH\cdot CS\cdot SK$, which forms white crystals, is highly sensitive to moisture or carbon dioxide, and when treated in aqueous solution with a mineral acid yields an oily compound, possibly μ-mercaptolthiazoline, $CHMe_2\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot S\\ NH\cdot CS\end{matrix}$ (compare Knorr and Rössler, A., 1903, i, 465).

N-*Dimethylleucine ethyl ester*, obtained by treating racemised *l*-α-bromo*iso*hexoic acid with dimethylamine solution, evaporating to dryness in a vacuum, and passing dry hydrogen chloride through the absolute alcoholic solution of the residue, forms a pale yellow liquid, b. p. 195—199° (impure). Free N-*dimethylleucine*, $C_8H_{17}O_2N$, forms dazzling, white crystals, m. p. 185°, lævorotatory in aqueous solution.

N-*Dimethylleucinol*, $C_8H_{19}ON$, prepared by reducing *N*-dimethylleucine ethyl ester by means of alcohol and sodium, has b. p. 192—195°, and when treated with methyl iodide yields

Leucinol-choline methiodide, $CHMe_2\cdot CH_2\cdot CH(CH_2\cdot OH)\cdot NMe_3I$,

which crystallises in slender needles, m. p. 138—139°. The corresponding *quaternary ammonium base* forms a tenacious, non-crystalline, highly hygroscopic mass; the *picrate*, $C_{15}H_{24}O_8N_4$, lanceolate crystals, m. p. 136°, and the *chloride*, $C_9H_{22}ONCl$, shining, white needles, m. p. 173°.

N-*Dimethylphenylalanine ethyl ester*, $C_{13}H_{19}O_2N$, prepared from α-bromo-β-phenylpropionic acid and dimethylamine, forms a highly viscous, colourless oil, b. p. 130—134°/8 mm.

N-*Dimethylphenylalaninol*, $CH_2Ph{\cdot}CH(NMe_2){\cdot}CH_2{\cdot}OH$, has b. p. 151°/14 mm.

Phenylalaninol-choline iodide, $CH_2Ph{\cdot}CH(NMe_3I){\cdot}CH_2{\cdot}OH$, forms white crystals, m. p. 200°, and the corresponding *chloride*, crystals, m. p. 194°.

Phenylalaninol, $CH_2Ph{\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH$, forms a viscous, yellow oil, b. p. 110—130°/2—3 mm., which slowly undergoes partial crystallisation. The *hydrochloride*, $C_9H_{14}ONCl$, crystallises in white, drusy masses, m. p. 128°.

dl-*Alaninol*, $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}OH$, is a liquid, b. p. 173—176°, with a basic odour.

The product obtained by hydrolysing casein, esterifying the resulting mixture of amino-acids, acetylating the esters, and then reducing by means of sodium and alcohol, appears to contain colamine, alaninol, valinol, leucinols, phenylethylalaninol, etc.

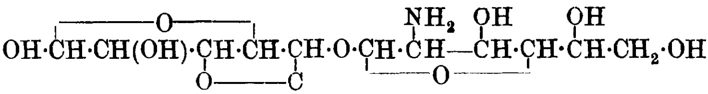
T. H. P.

The Oxidation of Cystine and other Amino-acids in Contact with Blood Charcoal. OTTO WARBURG and ERWIN NEGELEIN (*Biochem. Zeitsch.*, 1921, **113**, 257—284).—In the oxidation of these amino-acids in contact with blood charcoal, the following results were obtained: Cystine used up oxygen 32% and produced carbon dioxide 20%, ammonia 29% and sulphuric acid 11%. Cysteine in the same circumstances used up oxygen 29% and produced carbon dioxide 22%, ammonia 30% and sulphuric acid 18%. Leucine used up oxygen 16% and produced carbon dioxide 17% and ammonia 74%. The figure in each case represents the percentage of the amount that would obtain in the complete combustion of the substance. Tyrosine was also oxidised on charcoal, but incompletely. The kinetics of the reactions as well as the influence of temperature are discussed.

S. S. Z.

The Chemical Structure of Chondridin. P. A. LEVENE and J. LÓPEZ-SUÁREZ (*J. Biol. Chem.*, 1921, **45**, 467—471).—Chondridin was isolated by Hebting (A., 1914, i, 888) on the hydrolysis of chondrotin sulphuric acid. Since, however, the accepted structural representation of the latter substance admits in the organic radicle of the molecule only one derivative of chondrosin, namely, the acetyl derivative, it seemed probable that Hebting's chondridin was formed from chondrosin through manipulation. The available evidence appeared to indicate that chondridin is a lactone

of chondrosin, and has probably the structure (the position of the NH_2-group is uncertain)



The experimental work which the present paper describes supports this theory.

Chondridin, $C_{12}H_{19}O_{10}N,2\frac{1}{2}H_2O$, forms a white, crystalline powder, darkens 200, $[\alpha]_D^{20} + 60{\cdot}6$. J. C. D.

Alkyl Cyanoacetic Esters. JOHN C. HESSLER and ROBERT M. LAMB (*J. Amer. Chem. Soc.*, 1921, **43**, 205—208. Compare A., 1916, i, 378).—Ethyl cyanoacetate, when ethylated in methyl alcoholic solution, gave *methyl α-cyano-α-ethylbutyrate*, b. p. 103—105°/23·5 mm.; 205—206°/743 mm.; D^{21} 0·977. With sodium *iso*amyloxide and *iso*amyl iodide in *iso*amyl alcoholic solution ethyl cyanoacetate gave iso*amyl α-cyano-δ-methyhexoate* and iso*amyl α-cyano-δ-methyl-α-*iso*amylhexoate*, from which *α-cyano-δ-methyl-α-*iso*amylhexoic acid*, m. p. 74–75°; D^{22} 0·9074, giving a *silver* salt, was obtained. W. G.

Simple Cyanic and Cyanuric Compounds. II. Cyanuric Triazide, C_3N_{12}. ERWIN OTT and ERNST OHSE (*Ber.*, 1921, **54**, [*B*], 179–186. Compare A., 1919, i, 260).—Cyanuric triazide is prepared by the very gradual addition of finely powdered cyanuric chloride to a well-stirred, ice-cold aqueous solution of sodium azide or, more conveniently, from the same substances dissolved in aqueous acetone. It forms colourless, highly refractive crystals, m. p. 94°, D_{13}^{13} 1·54 (after solidification from the molten condition). It explodes when heated for some time at 150—160°, or for a shorter period at 170—180° with sensible previous evolution of gas, and is sensitive to blow or shock, but not to a greater extent than is mercury fulminate. In contrast with the behaviour of the azides of the heavy metals, large crystals of cyanuric triazide do not exhibit a much greater sensitiveness to shock than does the finely divided material. Nitrogen and cyanogen are the gaseous products formed when cyanuric triazide is exploded in a vacuum. The triazide is rapidly and completely hydrolysed by $N/10$ aqueous sodium hydroxide solution at 50°. The constitution of the compound is discussed at some length; its slight reactivity in comparison with the cyanuric haloids and cyanuric cyanide indicates that it may possibly be a cyanuric tritetrazole. For the present, however, it is regarded as a triazide, since its ready hydrolysis by alkali is otherwise very difficult to explain.

The action of sodium nitrite and dilute acid on cyanuric trihydrazide has been further examined (compare Finger, A., 1907, i, 298); the latter substance is most conveniently prepared by warming trimethyl cyanurate with an excess of hydrazine hydrate on the water-bath for several hours. Diazotisation of the second and particularly of the third hydrazine group is found to take place

so slowly, however, that it is impossible to prepare pure cyanuric triazide in this manner. The latter cannot be isolated by fractional crystallisation of the product of the reaction, since the solubilities of the intermediate products of the triazide appear to be closely similar and, in addition, the substances form mixed crystals.

H. W.

Reactions of Mercury Fulminate with Sodium Thiosulphate. F. H. DUPRÉ and P. V. DUPRÉ (*Analyst*, 1921, **46**, 42—49).—Boric acid may be used in place of potassium iodide to prevent loss of alkalinity when mercury fulminate is decomposed by sodium thiosulphate. Ammonia is one of the products of the decomposition, and the following equations are suggested to explain the course of the reaction: $Hg(CNO)_2 + 2Na_2S_2O_3 = HgS_4O_6 + NaCN + NaOCN + H_2O + 2NaOH = HgSO_4 + 2Na_2SO_4 + NaSCN + H_2O$; $NaSCN + 3H_2O = NH_3 + H_2S + CO_2 + NaOH$; $HgSO_4 + H_2S = HgS + H_2SO_4$; $H_2SO_4 + NaOH + NaSCN = Na_2SO_4 + HCNS + H_2O$; $HCNS + NH_3 = NH_4{\cdot}CNS$. The authors also discuss the precautions to be observed when large quantities of fulminate are to be destroyed by treatment with thiosulphate solution.

W. P. S.

The Preparation and some Physical Constants of Cyanogen Chloride. CH. MAUGUIN and L. J. SIMON (*Ann. Chim.*, 1921, [ix], **15**, 18—41).—The authors have examined different methods for the preparation of cyanogen chloride and find that the best yield is obtained by the action of chlorine on hydrocyanic acid (compare Price and Green, A., 1920, i, 425). The physical constants given are b. p. 12·5°/755 mm.; m. p. − 7° to − 6°; D^0 1·222 with an average expansion coefficient between 0° and 45° of 0·0015.

W. G.

The Bismuthobromocyanides; New Complex Compounds. A. CH. VOURNAZOS (*Compt. rend.*, 1921, **172**, 535—537).—Bismuth bromide reacts with metallic cyanides in the absence of moisture and in the presence of dry xylene when warmed on a water-bath to give complex cyanides in which the bismuth is masked in the complex ion. The following have been prepared, *potassium bismuthobromocyanide*, $K_3BiBr_3(CN)_3$, *silver bismuthobromocyanide*, $Ag_3BiBr_3(CN)_3$; *cuprous bismuthobromocyanide*, $Cu_3BiBr_3(CN)_3$; and *mercury bismuthobromocyanide*, $Hg_3Bi_2Br_6(CN)_6$. All these complex compounds are decomposed by water at the ordinary temperature.

W. G.

Catalytic Action of Hydrogen Peroxide on Potassium Ferro- and Ferri-cyanides. E. A. LÜCK (*Apoth. Zeit.*, 1921, **36**, 18—19; from *Chem. Zentr.*, 1921, **1**, 401—402. Compare A., 1919, **1**, 389).—Further investigation has shown that the compounds $H_8Fe_2(CN)_{12}$ and $H_6Fe_2(CN)_{12}$ belong to the ferri- and ferro-series, and hence are to be termed octahydroferricyanic and hexahydroferrocyanic acids respectively. The constitution assigned previously to the latter is thus confirmed. The following salts of

octahydroferricyanic acid are described; *potassium, calcium, copper, platinum, mercuric, uranyl, silver, iron*. The following salts are described of hexahydroferrocyanic acid: *potassium, calcium, copper, platinum, mercuric, uranyl, silver, iron*. All these salts are anhydrous. H. W.

Possible Asymmetry of Aliphatic Diazo-compounds. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1921, **45**, 593—594).—Preliminary results on diazosuccinic esters indicate the possibility of asymmetry in such compounds. J. C. D.

1 : 1-Dimethyl*cyclo*hexane from Methylheptenone. ARTHUR WILLIAM CROSSLEY and NORA RENOUF (T., 1921, **119**, 271—275).

Some Retropinacolic Transpositions. (MLLE) JEANNE LÉVY (*Compt. rend.*, 1921, **172**, 383—385).—Further evidence is given in support of Tiffeneau's hypothesis as to the mechanism of these transpositions, which occur during the dehydration of unsymmetrical trisubstituted primary or secondary alcohols (A., 1906, i, 662). $\gamma\gamma$-Diphenylbutan-β-ol, $CMePh_2{\cdot}CHMe{\cdot}OH$, when distilled at the ordinary temperature with porous earth, gives $\beta\gamma$-diphenyl-Δ^{β}-butene, $CMePh{:}CMePh$. $\gamma\gamma$-Diphenylpentan-β-ol, $CEtPh_2{\cdot}CHMe{\cdot}OH$, by simple distillation yields $\beta\gamma$-diphenyl-Δ^{β}-pentene, $CEtPh{:}CMePh$. $\alpha\beta$-Diphenyl-β-methylpropanol,

$$CH_3{\cdot}CMePh{\cdot}CHPh{\cdot}OH,$$

gives $\gamma\gamma$-diphenyl-β-methyl-Δ^{β}-propene, $CPh_2{:}CMe_2$, and $\alpha\beta\beta$-triphenylpropanol, $CMePh_2{\cdot}CHPh{\cdot}OH$, gives $\alpha\alpha\beta$-triphenyl-Δ^{α}-propene, $CPh_2{:}CPhMe$. W. G.

Influence of Substituents on Reactions. I. Influence of Chlorine and Bromine on the Velocity of Interaction of Benzyl Chloride with Sodium Ethoxide. HARTWIG FRANZEN and IRENE ROSENBERG (*J. pr. Chem.*, 1920, [ii], **101**, 333—340. Compare A., 1920, i, 730).—Introduction of chlorine into the nucleus of benzyl chloride increases its reactivity, the order $p > m > o$ expressing the influence of orientation; bromine increases reactivity in the meta-, but diminishes it in the ortho-position. But the variation in the influence of the halogen atom in this case, as in those of the reduction of phenylhydrazine, and the formation of picrates of hydrocarbons and phenols (A., 1918, i, 456) are slight. The results are discussed in connexion with those previously obtained from the methyl group. J. K.

Preparation and Properties of 1 : 3 : 5-Trinitrobenzene. L. GUY RADCLIFFE and ALAN A. POLLITT (*J. Soc. Chem. Ind.*, 1921, **40**, 45—48T.).—In general, nitration of 1 : 3-dinitrobenzene yields the known 1 : 3 : 5-trinitro-compound, m. p. 121°, but occasionally a trinitrobenzene, m. p. 61°, is formed, although this is not obtainable at will. This new compound is convertible by simple reactions into that melting at 121° and appears to be a less stable form of *s*-trinitrobenzene.

The highest yield, namely 71%, of the compound, m. p. 121°,

was obtained by adding 50 grams of 1 : 3-dinitrobenzene gradually to a mixture of 75 grams of nitric acid (100%) and 125 grams of oleum (60% of SO_3) heated in a reflux apparatus at 110°, 50 grams of the oleum and 35 grams of the nitric acid being afterwards added and the whole heated at 110—120°; the total duration of the nitration amounts to six hours. In blue light lower yields are obtained than in white light.

The influence of various catalysts was examined, but these failed to determine formation of the compound, m. p. 61°. The properties of the two forms are similar, but the unstable one reacts much the more slowly with sodium hydrogen carbonate in alcoholic solution and, further, cannot be sublimed. The additive compounds formed with aniline both have m. p. 124° and yield the trinitrobenzene, m. p. 121°, when treated with dilute hydrochloric acid. With α-(or β-)naphthylamine both form the same additive compound, m. p. 214° (162°) (see Sudborough, T., 1901, **79**, 522), which yields the stable *s*-trinitrobenzene on decomposition. The unstable is not converted into the stable form when heated, either alone or in concentrated sulphuric acid, just above its melting point, but fractional crystallisation of a mixture in equal volumes of the saturated alcoholic solutions of the two forms yields only that with m. p. 121°.

The two modifications have the same molecular weight in solution and yield the same dinitroaniline, the same nitrophenylenediamine, and the same triaminobenzene. Experiments made with benzene as solvent according to the method suggested by Sidgwick (T., 1915, 672) indicate that the two forms are polymorphic.

T. H. P.

The Nitrotoluenes. V. Binary Systems of *o*-Nitrotoluene and another Nitrotoluene. JAMES M. BELL, EDWARD B. CORDON, FLETCHER H. SPRY, and WOODFORD WHITE (*J. Ind. Eng. Chem.*, 1921, **13**, 59—61. Compare A., 1920, i, 22, 23, 152, 153).—The results are recorded of work on three binary systems in each of which *o*-nitrotoluene is one of the components, and *p*-nitrotoluene, 2 : 4-dinitrotoluene, or 2 : 4 : 6-trinitrotoluene is the other component. The existence of two different crystalline forms of *o*-nitrotoluene is confirmed; the metastable α-form always appears first, and frequently remains unchanged for several hours, even when the freezing liquid is stirred vigorously. A simplified method for the transformation of the metastable to the stable β-form is based on an observation made in an attempt to obtain the eutectic temperature for *p*-nitrotoluene and α-*o*-nitrotoluene. The determination of this eutectic point failed as a result of the change from the metastable form to the stable form, and the latter was prepared, therefore, by seeding liquid *o*-nitrotoluene at − 10° with a few crystals from this mixture. The temperature immediately rose to − 4·45° (corr.) and remained constant to complete solidification. In the binary system *p*-nitrotoluene–*o*-nitrotoluene the eutectic point and composition are − 15·73° and 26% *p*-nitrotoluene; in the system 2 : 4-dinitrotoluene–

o-nitrotoluene, $-11{\cdot}45°$ and 21% of 2:4-dinitrotoluene; and in the case of the system 2:4:6-trinitrotoluene–*o*-nitrotoluene it was possible to follow out curves both for the α-form and for the β-form of *o*-nitrotoluene to their respective eutectic points with trinitrotoluene; thus in the system with the β-form the eutectic point and composition are $-9{\cdot}7°$ and 19·5% of trinitrotoluene, and in the system with the α-form $-15{\cdot}6°$ and 16% of trinitrotoluene. F. M. R.

Melting Points of Mixtures of *o*- and *p*-Toluenesulphonyl Chlorides. LEONARD HARDING (T., 1921, **119**, 260—262).

Solubility of the Isomeric Nitroanilines in *m*-Xylene. CHAPAS (*Compt. rend.*, 1921, **172**, 538—539).—One hundred grams of *m*-xylene at 15° dissolves 11·6 grams of *o*-nitroaniline, 1·74 grams of *m*-nitroaniline, or 0·28 gram of *p*-nitroaniline. There is an indication that these nitroanilines form additive compounds with *m*-xylene having the composition $C_6H_4(NH_2){\cdot}NO_2+C_6H_4Me_2$. W. G.

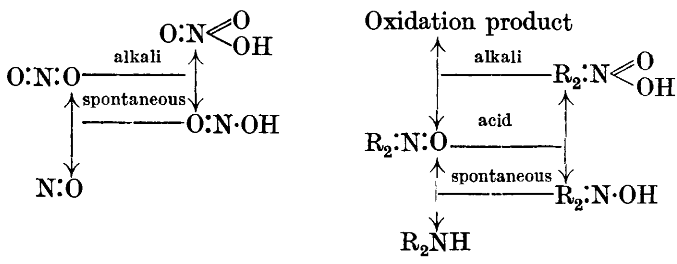
Optically Active α-Amino-αβ-Diphenylethanes. RAGNAR SÖDERQUIST (*J. pr. Chem.*, 1920, (ii), **101**, 293—307).—The resolution of this base has been repeated, since Strandmark's account (*Svensk. Kem. Tidskr.*, 1906, **18**, 3) is only slight. The *r*-base, from the reduction of deoxybenzoinoxime, b. p. 165°/11 mm.; 170°/14° mm.; 181°/25 mm.; 188°/32 mm.; 222°/75 mm., gives an *acetate*, $C_{16}H_{19}O_2N$, m. p. 137·5—138·5° (corr.). The lævo-base was separated from the racemic compound in the form of its *normal* (compare Strandmark, *loc. cit.*) *tartrate*, $C_{32}H_{36}O_6N_2$, m. p. 220—221° (decomp.), $[\alpha]_D^{20}-43°$; *hydrochloride*, $C_{14}H_{15}N,HCl,H_2O$, m. p. above 250°, $[\alpha]_D^{15}-70°$; *hydrogen tartrate*, $C_{18}H_{21}O_6N$, m. p. 160° (corr. decomp.), precipitated from alcoholic solution; *normal malate*, $C_{32}H_{36}O_5N_2,H_2O$, m. p. 171°, $[\alpha]_D^{20}-70°$; *hydrogen malate*, $C_{18}M_{21}O_5N,\frac{1}{2}H_2O$, m. p. 139—140° (corr.), $[\alpha]_D^{20}-56°$; *carbamide*, $C_{15}H_{16}ON_2$, m. p. 109—110° (corr.); $[\alpha]_D^{15}-21°$. The dextro-base, m. p. 15° (*ca.*), b. p. 168°/15 mm., $[\alpha]_D^{15}+11{\cdot}04°$, shows a tendency to racemisation above 200°, and was obtained from the *r*-base, after removal of the lævo-compound, as the *normal malate*, $C_{32}H_{36}O_5N_2$, m. p. 199·5—200° (decomp.), $[\alpha]_D^{20}+65°$; *normal tartrate*, $C_{32}H_{36}O_6N_2,2H_2O$, m. p. 201·5—202° (decomp.), $[\alpha]_D^{20}+68°$; *hydrogen tartrate*,

$$C_{18}H_{21}O_6N,\tfrac{1}{2}H_2O,$$

m. p. 159—160° (corr.), $[\alpha]_D^{20}+56°$; *acetyl* derivative, $C_{16}H_{17}ON$, m. p. 168·5°, $[\alpha]_D^{20}-15°$. J.K.

Steps in the Reduction of Aryl Derivatives of Nitric Acid. KURT H. MEYER and WALTER REPPE (*Ber.*, 1921, **54**, [*B*], 327—337).—It has been shown by Meyer and Gottlieb-Billroth (A., 1920, i, 37) that the quinonoid salts of diarylhydroxylamine *N*-oxides are converted by gentle reduction into diarylnitric oxides and by complete reduction into the corresponding amines. The course of the reaction has now been followed more closely and the decomposition of the free diarylhydroxylamine *N*-oxides has been investigated.

The quinonoid salts are more or less rapidly converted by alkali hydroxide in aqueous solution or by dry alkali in chloroform solution into oxonium hydroxides, which speedily pass into diarylhydroxylamine *N*-oxides; the latter, however, immediately decompose into diarylnitric oxides and products which have not yet been identified. Moderated reduction of the quinonoid salts by zinc dust and alcohol or sodium iodide and acetone leads smoothly to the diarylnitric oxides, of which a series of new examples is given; these substances are stable towards alkali, but very sensitive to acid, giving, on the one hand, the quinonoid salt with quinquevalent nitrogen, and, on the other, the corresponding *N*-diarylhydroxylamine (the latter is gradually decomposed into amine and nitric oxide). The diarylnitric oxides are converted by halogen into the quinonoid salts with quinquevalent nitrogen; they are reduced by hydrazine hydrate or phenylhydrazine to *N*-diarylhydroxylamines, which speedily pass when dissolved, more slowly when preserved in the dry condition, into the corresponding amine and nitric oxide, $3R_2N\cdot OH \longrightarrow 2R_2NO + R_2NH + H_2O$. Acid reducing agents convert all the intermediate products into diarylamines, from which they cannot be regenerated by oxidation, this process leading to coloured solution of the salts of the corresponding tetra-arylhydrazines. The course of reduction exhibits close similarity to that of nitric acid, as shown in the annexed scheme, the only difference being that the diarylnitric oxides as bases are stable in acid but unstable in alkaline solution, whilst the inorganic substances, as acids, are stable in alkaline but decomposable in acid solution.



The following individual substances are described: di-*p*-anisylnitric oxide, m. p. 150° (decomp.), after softening at 120°; *di*-p-*anisylhydroxylamine* N-*oxide perbromide*, coppery crystals, m. p. 116° (decomp.), which is reduced quantitatively by aqueous sodium iodide to di-*p*-anisylamine, m. p. 101°; *di*-p-*anisylhydroxylamine*, colourless needles, m. p. 118°, to a brownish-red liquid, after becoming discoloured from 60°; 4 : 4′-*dimethoxy*-2 : 6 : 2′ : 6′-*tetramethyldiphenylnitric oxide*, red crystals, m. p. 163° 4 : 4′-*dimethoxy*-2 : 6 : 2′ : 6′-*tetramethyldiphenylamine*, m. p. 128°; *quinonoid periodide* of 2 : 4 : 2′ : 4′-*tetramethoxydiphenylhydroxylamine* N-*oxide*, steel-blue needles, m. p. 124° decomp.); *quinonoid perchlorate* of 2 : 4 : 2′ : 4′-*tetramethoxydiphenylhydroxylamine*, dark blue crystsls, m. p. 175° (decomp.); *diperchlorate* of *octamethoxytetraphenyl*-

hydrazine, $N_2[C_6H_3(OMe)_2]_4,(HClO_4)_2$, pale blue needles, m. p. 194·5° (decomp.); 4 : 6 : 4′ : 6′-*tetramethoxy*-2 : 2′-*dimethyldiphenylnitric oxide*, $NO[C_6H_2Me(OMe)_2]_2$, red prisms, decomp. 175°; *quinonoid perbromide* of 4 : 6 : 4′ : 6′-*tetramethoxy*-2 : 2′-*dimethyldiphenylhydroxylamine* N-*oxide*, black needles; 4 : 6 : 4′ : 6′-*tetramethoxy*-2 : 2′-*dimethyldiphenylhydroxylamine*, m. p. (in crude condition) 145°; 2 : 4 : 6 : 2′ : 4′ : 6′-*hexamethoxydiphenylnitric oxide*, tile-red crystals, decomp. 194°. H. W.

Catalytic Preparation of Secondary Amines and Attempts at Alkylation of these Bases. ALPHONSE MAILHE (*Compt. rend.*, 1921, **172**, 280—283; *Bull. Soc. chim.*, 1921, [iv], **29**, 106—110).—Schiff's bases of the type CHR:NR′ may be readily converted into the corresponding secondary bases by suspending in the liquid at 170° a little finely divided nickel and passing in a current of hydrogen. This method has been successfully applied to the benzylidene derivatives of aniline, *o*-, *m*-, and *p*-toluidine, and *p*-anisidine.

Attempts to prepare tertiary amines from these secondary amines, by passing their vapour along with that of methyl or ethyl alcohol over aluminium oxide at 380—400°, were not successful. Under these conditions phenylbenzylamine and methyl alcohol gave formaldehyde, toluene, and methyl- and dimethyl-aniline. *p*-Tolylbenzylamine and ethyl alcohol gave formaldehyde, toluene, and ethyl- and diethyl-*p*-toluidines. W. G.

The Thiocarbimide Reaction. I. SHITARÔ KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 951—965).—On boiling phenylethylammonium phenylethyldithiocarbamate with alcohol, hydrogen sulphide was evolved, and *s*-diphenylethylthiocarbamide, m. p. 88°, was formed; this was treated with concentrated hydrochloric acid to obtain thiocarbimide, but without success. By condensation, with carbon disulphide in the presence of sodium hydrogen carbonate in absolute alcoholic solution, leucine, phenylalanine, and tyrosine yield the corresponding *s*-di-*a*-thiocarbamic acids, hydrogen sulphide being evolved in theoretical quantity. This reaction can be utilised for the estimation of these amino-acids. Glycine, sodium glutamate, and hystidine monohydrochloride do not, however, condense with carbon disulphide by this method. Sodium thiocyanoacetate gives 2 : 4-diketothiazolidine when heated with concentrated hydrochloric acid, whilst the reaction product of sodium α-chloro*iso*hexoate and potassium thiocyanate is a sulphur compound, m. p. 132°, which may perhaps be 2 : 4-diketo-5-*iso*-butylthiazolidine. The following substances were obtained by condensation: r-s-α-*Thiocarbodiamino*isohexoic *acid*, transparent, pale yellow solid, and its *calcium* and *barium* salts, from leucine. l-s-α-*Thiocarbodiamino*-β-*phenylpropionic acid* and its *barium* salt from phenylalanine. The corresponding acid from tyrosine was not obtained in the pure state. K. K.

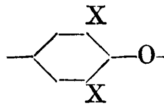
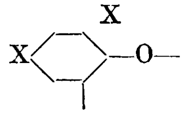
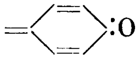
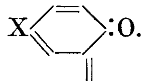
The Interaction of Tin and Phenol. HARPER F. ZOLLER (*J. Amer. Chem. Soc.*, 1921, **43**, 211—212).—When phenol is slowly distilled in the presence of tin it is partly decomposed, giving benzene, and the tin is converted into stannic oxide. At the ordinary temperature, the velocity of reaction is so slow as to be practically negligible. W. G.

A Catalytic Decomposition of certain Phenol Silver Salts. III. The Action of Mercury on Tribromophenol Bromide. W. H. HUNTER and G. H. WOOLLETT (*J. Amer. Chem. Soc.*, 1921 **43**, 131—135. Compare A., 1916, i, 717; 1918, i, 63).—When tribromophenol bromide in benzene solution is shaken with mercury it yields polydibromophenylene oxide (*loc. cit.*), the mercury removing two bromine atoms and the same unsaturated residue, $C_6H_2OBr_2$, being formed as results from the catalytic decomposition of the silver salts of tribromophenol. This is also apparently the compound obtained by Kastle and Loevenhart (A., 1902, 211) by the action of sunlight on a solution of tetrabromo*cyclo*hexadienone on carbon disulphide.

Benedikt's hexabromodiphenoquinone (A., 1879, 717) is not obtained by the action of tribromophenol bromide on silver tribromophenoxide as claimed by Kastle and Loevenhart (*loc. cit.*). The silver salt is catalytically decomposed by bromine, resulting from the slow spontaneous decomposition of the tribromophenol bromide. W. G.

A Catalytic Decomposition of certain Phenol Silver Salts. IV. The Constitution of the Amorphous Oxides. W. H. HUNTER and G. H. WOOLLETT (*J. Amer. Chem. Soc.*, 1921, **43**, 135—151. Compare preceding abstract).—*Potassium tri-iodophenoxide* crystallises from alcoholic solution with one molecule of alcohol. In the presence of a trace of bromine or in bright sunlight alone in aqueous solution, it is converted into the purple *chromo*-polydi-iodophenylene oxide (compare Lautemann, *Annalen*, 1861, **120**, 309). *Potassium tribromophenoxide* behaves similarly. When tested by their behaviour towards alkaline hydrazine solutions, neither the polydi-iodo- nor the polydibromo-phenylene oxide showed the presence of more than traces of quinonoid oxygen. *chromo*-Polydi-iodophenylene oxide on reduction gave a colourless *compound*, which yielded an *acetyl* derivative. The latter on hydrolysis gave a colourless compound which on oxidation gave the original red chromo-compound, all these compounds being amorphous. The colourless reduction compound, its acetyl derivative and the product of hydrolysis of the latter, when tested, did not show the presence of any quinonoid oxygen.

The amorphous oxides resulting from the catalytic decomposition of symmetrically trihalogenated phenol salts occur in two isomeric forms, one colourless and the other coloured. The colourless ones are apparently mixtures, made up of varying numbers of residues

of the type  and  linked together. The coloured ones contain in addition residues of the type  and  Thus no definite structures can be assigned to these polymerised compounds, which must be considered as " piles " of residues. W. G.

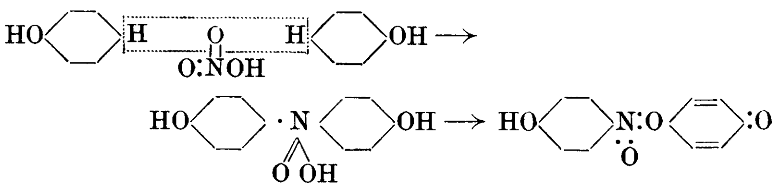
A Catalytic Decomposition of certain Phenol Silver Salts. V. The Action of Iodine on the Sodium Salt of Trichlorophenol. W. H. HUNTER and LILLIAN M. SEYFRIED (*J. Amer. Chem. Soc.*, 1921, **43**, 151—159. Compare preceding abstracts).—The action of iodine on the sodium salt of trichlorophenol apparently results in the following series of changes. The iodine removes the sodium atom forming sodium iodide, and leaves an unsaturated residue, $C_6H_2OCl_3$. The latter loses an atom of chlorine, which expels the iodine from the sodium iodide, whilst the new unsaturated residue polymerises, forming polydichlorophenylene oxide $(C_6H_2OCl_2)_n$. W. G.

Rate of Reaction of Picric Acid with Nitrating Acid. D. L. HAMMICK (*J. Soc. Chem. Ind.*, 1921, **30**, 26T).—Even at a relatively high temperature (96° to 115°), the rate of destruction of picric acid by nitrating acids is too slow to affect the yield obtained by the nitration of phenol. W. P. S.

Phenolic Hexamethylenetetramine Compounds. MORTIMER HARVEY and L. H. BAEKELAND (*J. Ind. Eng. Chem.*, 1921, **13**, 135—141).—The authors have prepared the additive products hexamethylenetetramine -triphenol, -di-*m*-cresol, -di-*p*-cresol, -mono-*o*-cresol, -quinol, -resorcinol, and -carvacrol. The compounds are crystalline substances having no definite melting point; when heated to near their point of liquefaction, they decompose partly and are converted into resinous substances. W. P. S.

Urethanes of Thymol and Carvacrol. D. C. L. SHERK. (*Amer. J. Pharm.*, 1921, **93**, 115—125).—The following urethanes were prepared by heating thymol or carvacrol with various aromatic carbimides in the presence of petroleum (b. p. 170—200°) : thymyl phenylurethane, m. p. 106·5—107°; carvacryl phenylurethane, m. p. 138°; hydrothymoquinone phenyldiurethane, m. p. 229—230°; thymyl α-naphthylurethane, m. p. 156—157°; carvacryl α-naphthylurethane, m. p. 117—119°. By dissolving hydrothymoquinone in a slight excess of 15% sodium hydroxide solution and adding a quantity of benzoyl chloride sufficient to leave an odour after the completion of the reaction, dibenzoylhydrothymoquinone was obtained, m. p. 141—142°. W. P. S.

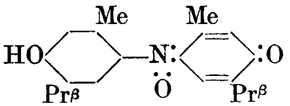
Action of Nitric Acid on Phenols and Phenol Ethers. KURT H. MEYER and W. E. ELBERS (*Ber.*, 1921, **54**, [*B*], 337—346. —In general, the reactions of phenol ethers are very similar to those of phenols, so that the latter might be expected to yield quinonoid salts under the action of nitric acid thus :



(compare A., 1920, i, 37). The only substance of this type obtained previously appeared to be 7-hydroxyphenoxaz-2-one *N*-oxide prepared by the action of fuming nitric acid and ether on resorcinol. It is now shown, however, that a series of such products can be derived from monohydric and dihydric phenols. Kinetic measurements appear to indicate that the reaction is trimolecular, and therefore that the indophenol oxide is formed directly from the phenol (2 mols.) and nitric acid (1 mol.). In confirmation, it is shown directly that neither the nitro- nor the nitroso-phenol can be an intermediate product. The behaviour of phenols and their ethers towards nitric acid is therefore closely analogous, two concurrent reactions taking place, one of which leads to the production of the nitro-compound, the other to the formation of the indophenol oxide. The predominance of one or other type of change appears to depend on the nature of the substituents. The possibility of explaining the reactivity of phenols by the formation of a ketonic form (compare Henshelwood, T., 1919, **115**, 1180) seems to be excluded.

Indophenol-N-*oxide*, $HO\cdot C_6H_4\cdot NO\colon C_6H_4\colon O$, brownish-red crystals, which become carbonised when heated without exhibiting a definite melting point, is prepared by the gradual addition of pure, colourless concentrated nitric acid to a solution of phenol in glacial acetic and concentrated sulphuric acids at 15—20° ; the dark violet solution is poured into ice water and the product immediately extracted with ether. It is purified by conversion into the reddish-violet hydrochloride, from which it is recovered by hydrolysis with ice-cold water. It is reduced by sodium hyposulphite or by zinc dust and acetic acid in the presence of chloroform to 4-dihydroxydiphenylamine, which is oxidised by air to indophenol, m. p. 160°. O-*Benzoylindophenol* N-*oxide* crystallises in orange-yellow or brown leaflets, m. p. 174·3°. Similar treatment converts *o*- and *m*-cresol into the reddish-violet *hydrochlorides* of the corresponding indophenol oxides, the yields being about the same as with phenol (0·6 gram from 20 grams); *p*-cresol, on the other hand, merely gives a dirty brown coloration. *m-Xylenol* yields a dark green *hydrochloride*; the free indophenol oxide gives a dark greenish-blue

solution in dilute alkali. In a similar manner, thymol is converted into 2 : 2′-*dimethyl*-5 : 5′-*di*iso*propylindophenol* N-*oxide hydrochloride*, green crystals, m. p. 110° (decomp.), and 2 : 2′-*dimethyl*-5 : 5′-*di*iso*propylindophenol* N-*oxide*, red leaflets with green superficial colour, m. p. 168° (annexed formula).



7-*Methoxyphenoxaz-2-one* N-*oxide*, $OMe{\cdot}C_6H_3{<}{\overset{-O-}{\underset{NO}{}}}{>}C_6H_3{:}O$, dark brownish-red needles, m. p. about 252° (decomp.), is prepared from resorcinol monomethyl ether and yields an unstable di*hydrochloride* and a stable *monohydrochloride*. It is reduced by warm alkaline hyposulphite to the corresponding autoxidisable *amine*, and by phenylhydrazine or hydriodic acid dissolved in glacial acetic acid to 7-*methoxyphenoxazone*, tile-red needles, m. p. 247° (*hydrochloride*, dark red crystals, decomp. 170°); the latter cannot be re-converted into the oxide by treatment with nitrous or nitric acids, lead peroxide, or hydrogen peroxide in glacial acetic acid. H. W.

Tautomerism of Phenols. III. Sodium Hydrogen Sulphite and Phloroglucinol. WALTER FUCHS (*Ber.*, 1921, **54**, [*B*], 245—249).—In continuation of previous work (A., 1920, i, 159, 545), the author has now examined the behaviour of sodium hydrogen sulphite towards phloroglucinol, the latter substance being of particular interest in this connexion, since its tautomeric behaviour has been definitely established in other ways. The substances slowly unite when heated in aqueous solution on the water-bath and the *mono*-derivative, $C_6H_7O_6SNa$, is readily obtained in the pure condition and in good yield. The product closely resembles the compounds obtained previously from sodium hydrogen sulphite and phenols; thus, only traces of sulphur dioxide can be detected in its aqueous solution by means of iodine, and it is stable towards mineral acids. Its remarkable stability towards alkali, however, appears to indicate that it may be a sulphonic acid, but this behaviour is somewhat discounted by the observation that a considerable portion of the added sulphur dioxide is eliminated as barium sulphate when it is treated with neutral barium chloride solution in the presence of hydrogen peroxide; under these conditions, sodium dihydroresorcinolsulphonate is unaffected. It does not appear to be possible at present to decide between the alternative formulæ with the groups $CH_2{\cdot}C(OH){\cdot}O{\cdot}SO_2Na$ and $CH_2{\cdot}C(OH){\cdot}SO_3Na$.

Additive products of phloroglucinol with more than one molecule of sodium hydrogen sulphite are also formed, but have not been isolated in the pure condition owing to the small amount of phloroglucinol available. H. W.

Tautomerism of Phenols. IV. WALTER FUCHS (*Ber.*, 1921, **54**, [*B*], 249—252).—The resorcinol bisulphite compounds of Fuchs and Elsner (A., 1920, i, 545) have been considered by Bucherer (A., 1920, i, 732) to be sulphurous esters on account of

their stability towards mineral acids; the author points out that cyclic keto-bisulphite compounds are almost unknown and do not necessarily share the unstability of keto-sulphite compounds in general and that phloroglucinol bisulphite (preceding abstract), which is shown analytically not to be an ester, is as stable as Bucherer's esters. Bucherer's further contention that cyclic bisulphite compounds can be formed without co-operation of a ketonic group is admitted and, indeed, an example of this is presented by resorcinol, which can react with three molecular proportions of sodium hydrogen sulphite. The product formed in this manner cannot possibly be an ester, since the analyses show that water is not eliminated during its formation, and the validity of these data has not been questioned.

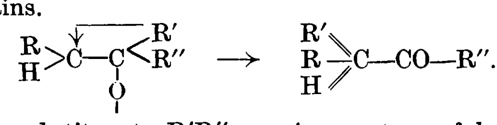
In reply to Herzig and Zeisel (A., 1920, i, 732), the author maintains that these chemists have not adduced experimental evidence in favour of the tautomerism of resorcinol, but have merely considered the possibility of it in connexion with their experiments on its ethylation. H. W.

Derivatives containing Sulphur prepared from Ethylene Chlorohydrin. EMIL FROMM and ADOLF KOHN (*Ber.*, 1921, **54**, [*B*], 320—326).—ββ′-*Dibenzoyloxydiethyl sulphide*, $S(C_2H_4{\cdot}OBz)_2$, colourless crystals, m. p. 65°, is obtained by the action of benzoyl chloride and sodium hydroxide on ββ′-dihydroxydiethyl sulphide, care being requisite that the mixture is kept cool and alkaline. The substance is oxidised by hydrogen peroxide in glacial acetic acid solution to ββ′-*dibenzoyloxydiethyl sulphoxide*, colourless needles, m. p. 83—85°, and by potassium permanganate to ββ′-*dibenzoyloxydiethylsulphone*, silvery leaflets, m. p. 95°. ββ′-Dibenzoyloxydiethyl sulphide is converted by bromine into ββ′-*dibenzoyloxydiethyl sulphide dibromide*, $SBr_2(C_2H_4{\cdot}OBz_2)_2$, yellow needles, m. p. 81°, which slowly decompose on exposure to moist air, and by iodine into the corresponding *di-iodide*, which, however, is very unstable. p-*Tolyl* β-*hydroxyethyl sulphide*, $C_6H_4Me{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 282—283°/atmosphere pressure (decomp.), 174°/30 mm. is prepared by the addition of ethylene chlorohydrin to a solution of *p*-tolyl mercaptan in concentrated aqueous sodium hydroxide; it yields a *benzoyl* derivative, m. p. 21°, b. p. 233°/15 mm., and is oxidised to p-*tolyl* β-*hydroxyethyl sulphoxide*, which, on account of the instability, could not be purified by distillation (*benzoate*, m. p. 106°). p-*Tolyl*-β-*hydroxyethylsulphone*, needles, m. p. 39°, b. p. 230°/13 mm., is obtained from ethylene chlorohydrin and sodium *p*-tolylenesulphinate. The corresponding *benzoate*, prepared by oxidation of the sulphide, or, preferably, by benzoylation of *p*-tolyl-β-hydroxyethylsulphone, crystallises in rods, m. p. 171°. p-*Tolyl* β-*benzoyloxyethyl sulphide dibromide*, m. p. 101°, is obtained from its components in glacial acetic acid or light petroleum solution and is hydrolysed smoothly by water to the sulphoxide, m. p. 106°, thus affording the readiest means of preparing the latter; the *di-iodide* forms wine-red crystals, m. p. 58—70°, which gradually loses iodine when preserved.

p-*Tolyl β-chloroethyl sulphide*, yellow, poisonous liquid, b. p. 255—257°/atmospheric pressure, 150°/22 mm., is prepared by the action of hydrogen chloride on a boiling alcoholic solution of *p*-tolyl-β-hydroxyethyl sulphide; it can be oxidised to the corresponding *sulphoxide* which decomposes when heated in a vacuum, and *sulphone*, colourless crystals, m. p. 71°. p-*Tolyl β-iodoethyl sulphide* is obtained as a red oil by the action of potassium iodide on a solution of the corresponding chloro-compound in absolute alcohol. H. W.

Condensation of *m*-Dimethylaminophenol with Benzaldehyde. SRI KRISHNA and FRANK GEO. POPE (T., 1921, **119**, 286—289).

The Pinacolic Nature of Transpositions in the α-Phenyl-β-methylpropane-αβ-diol Series. M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1921, **172**, 387—390).—When α-phenyl-β-methylpropane-αβ-diol is dehydrated by warming with dilute sulphuric acid it yields α-phenyl-α-methylpropaldehyde, $CMe_2Ph\cdot CHO$. The two methyl ethers derived from this glycol behave similarly. When dimethylstyrene oxide, $\begin{matrix}CHPh \\ | \\ CMe_2\end{matrix}\!\!>\!O$, is heated with zinc chloride or a trace of sulphuric acid it also yields α-phenyl-α-methylpropaldehyde. α-Phenyl-β-methylpropane αβ-iodohydrin, when treated with silver nitrate, loses the elements of hydrogen iodide and gives α-phenylethyl methyl ketone, $CHMePh\cdot COMe$. Thus in the transposition of trisubstituted glycols or their derivatives the nature of the migration depends on the nature of the substituents attached to the carbon atom carrying the oxygen which remains.



If of the substituents R′R″ one is an atom of hydrogen, the form of the reaction will depend on the nature of the second substituent. If the latter is an alkyl group, the hydrogen will migrate, but if it is an aryl group, then this aryl group will migrate. W. G.

4-Methylbenzophenone Chloride and its Condensation with Phenol. F. C. HAHN (*J. Amer. Chem. Soc.*, 1921, **43**, 175—179).—The condensation of 4-methylbenzophenone chloride with phenol is analogous to that between benzophenone chloride and phenol (compare Gomberg and Jickling, A., 1916, i, 29). When heated together in benzene solution, the two substances condense to give *diphenoxyphenyl*-p-*tolylmethane*, $C_6H_4Me\cdot CPh(OPh)_2$ m. p. 134°. If, however, the two substances react together at the ordinary temperature in the absence of a solvent, *phenyl*-p-*hydroxyphenyl*-p-*tolylcarbinol*, $C_6H_4Me\cdot CPh(OH)\cdot C_6H_4\cdot OH$, is obtained. This carbinol occurs in two desmotropic forms, which could not, however, be got in the pure state. If methylbenzophenone chloride

and phenol are heated together in the absence of a solvent the product is *phenyl-di*-p-*hydroxyphenyl*-p-*tolylmethane*. W. G.

Nitrobenzoates of the Three Cresols. EUGEN HÄNGGI (*Helv. Chim. Acta*, 1921, **4**, 23—25).—o-*Tolyl* o-*nitrobenzoate* forms aggregates of colourless, microscopic prisms, sintering at 64°, m. p. 68—69°; the m-*tolyl* ester, colourless, microscopic prisms, sintering at 56°, m. p. 58·5—60°; the p-*tolyl* ester, fern-like aggregates of colourless, microscopic, leaflets, softening at 77°, m. p. 78—79·5°. o-*Tolyl* m-*nitrobenzoate* forms scaly aggregates of colourless, microscopic, rhomboidal plates, softening at 94°, m. p. 96·5—97·5°; the m-*tolyl* ester, colourless, microscopic, rhomboidal plates with truncated points, softening at 61·5°, m. p. 63—64°; the p-*tolyl* ester, concentric bundles of flat prisms, m. p. 77—78°, softening several degrees lower. o-*Tolyl* p-*nitrobenzoate* forms feathery aggregates of colourless, microscopic needles, softening at 88·5°, m. p. 92—93°; the m-*tolyl* ester, bundles of colourless, microscopic needles, m. p. 85—85·5°; the p-*tolyl* ester, colourless, microscopic, quadrilateral, prismatic plates, m. p. 96·5—97·5°.

The phenylcarbamates of the three cresols have also been prepared and agree in properties with those obtained by Weehuizen (A., 1918, i, 341). T. H. P.

Preparation of *n*-Butyl *p*-Aminobenzoate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 148743).—*n*-Butyl *p*-aminobenzoate, prepared by the esterification of *p*-aminobenzoic acid with *n*-butyl alcohol in presence of gaseous hydrogen chloride, or by esterification of *p*-nitrobenzoyl chloride or *p*-nitrobenzoic acid with *n*-butyl alcohol by the usual methods and reduction of the resulting *n*-butyl *p*-nitrobenzoate, is a crystalline substance, m. p. 59°, b. p. 173—174°/8 mm., and very slightly soluble in water. n-*Butyl* p-*nitrobenzoate*, a substance not hitherto described, forms lamellar crystals, m. p. 35°, b. p. 160°/8 mm. G. F. M.

The Resolution of Aminophenylacetic Acid into its Optically Active Compounds. ST. MINOVICI (*Bul. Soc. Chim. România*, 1920, **2**, 8—13).—*r*-Aminophenylacetic acid gives a *benzoyl* derivative, m. p. 178°, which readily yields a *brucine* salt. This salt is resolved into its two components by fractional crystallisation and *brucine* d-*benzoylaminophenylacetate*, has m. p. 87—90°. From the latter salt d-*benzoylaminophenylacetic acid*, m. p. 187—188°; $[\alpha]_D^{15} + 84{\cdot}07°$, was obtained, which when boiled with 20% hydrochloric acid gave d-*aminophenylacetic acid*, sublimes at 227°, $[\alpha]_D^{15} - 90{\cdot}32°$. The corresponding *l*-compounds could not be obtained pure. W. G.

Benzilic Acid. J. HERZIG and MARIANNE SCHLEIFFER (*Annalen*, 1921, **422**, 326—332. Compare A., 1920, i, 846).—Acetylbenzilic acid, prepared by Klinger and Standke (A., 1889, 885) from benzilic acid and acetic anhydride, is formed also by the action on the acid of acetic anhydride and sodium acetate, but the latter colours the liquid and sometimes retards the subse-

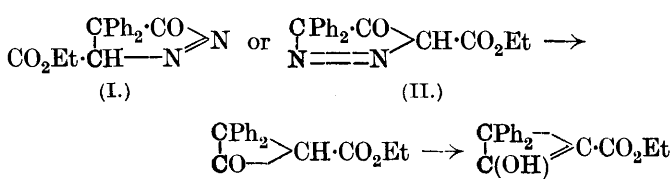
quent crystallisation of the compound. Molten acetylbenzilic acid remains unchanged at 140°, Klinger and Standke's statement that it decomposes with formation of benzilic acid at 100—110° being explainable by the presence of moisture in the preparation tested.

When treated with acetic anhydride, sodium acetate, and zinc dust, benzilic acid yields an acid, $C_{15}H_{14}O_2$, m. p. 144—146°, which is probably ββ-diphenylpropionic acid; the *methyl* ester has m. p. 56—59°. The reaction is explained simply by the equation, $OH\cdot CPh_2\cdot CO_2H + CH_3\cdot CO_2H = CO_2 + H_2O + CHPh_2\cdot CH_2\cdot CO_2H$, and is somewhat analogous to the action of acetic acid on α-ketonic acids (Homolka, A., 1885, 758). A distinct odour of aldehyde is, however, observable during the reaction, so that it is possible either that (1) acetaldehyde is formed by reduction of the acetic acid, carbon dioxide being liberated and benzhydrol formed as an intermediate product, or that (2) formic acid is first split off, formaldehyde and carbon dioxide being afterwards formed, together with benzophenone as intermediate product. Both these views are contradicted by the results obtained when benzophenone and benzhydrol are subjected to reducing acetylation. Benzophenone is not affected when treated with sodium acetate and acetic anhydride, but when zinc dust also is present benzopinacone is formed; benzhydrol gives, either in absence or in presence of zinc dust, acetylbenzhydrol.

Methyl benzilate, when boiled for an hour with acetic anhydride, sodium acetate, and zinc dust, remains almost entirely unchanged, only a small proportion of *methyl acetylbenzilate*, $CPh_2(CO_2Me_2)_2$, m. p. 122—125° being formed. T. H. P.

Ketens and Aliphatic Diazo-compounds. H. Staudinger and Th. Reber (*Helv. Chim. Acta*, 1921, 4, 3—23).—The interactions of aliphatic diazo-compounds and ketens have been investigated, partly with the hope of obtaining ketonic derivatives of the *cyclo*propane series, which should decompose similarly to tetraphenylethylenesulphone when heated, giving carbon monoxide and ethylene derivatives.

Diphenylketen and ethyl diazoacetate react energetically in the cold, liberating nitrogen quantitatively; the expected ethyl diphenyl*cyclo*propaneonecarboxylate (III) is, however, not obtained, the reaction being a complicated one. The initial product is probably an unstable pyrazolone derivative (I or II), which yields III, the latter undergoing rearrangement to ethyl *cyclo*propenolcarboxylate (IV):



(I.) (II.) (III.) (IV.)

Attachment of the diazoacetate at the carbonyl group of the diphenylketen formerly appeared improbable, but such reactions have now been realised with, for instance, phosphineimines (Staudinger and Meyer, A., 1920, i, 228). The unstable additive product (V or VI) gives an ethylene oxide derivative (VII) on decomposition :

$$\begin{array}{l}CPh_2\!:\!C\text{—}O\\ CO_2Et\cdot CH\cdot N\end{array}\!\!>\!N \quad \text{or} \quad \begin{array}{l}N\cdot C(CPh_2)\text{—}\\ N\cdot CH(CO_2Et)\end{array}\!\!>\!O \longrightarrow \begin{array}{l}CPh_2\!:\!C\text{—}\\ CO_2Et\cdot CH\end{array}\!\!>\!O$$

(V.) (VI.) (VII.)

The diazoacetic ester reacts in the same way with the carbonyl group of benzaldehyde, the ethylene oxide derivative in this case undergoing rearrangement into ethyl benzoylacetate (compare Schlotterbeck, A., 1907, i, 185, 676; 1909, i, 553). The ethyl diazoacetate appears to react more readily with the carbonyl group than with the carbon double linking, since twice as much of compound VII is obtained as of compound IV; the two together are obtained in 50—60% yield, various secondary products of unknown constitution being also formed.

*Ethyl diphenyl*cyclo*propenolcarboxylate* (IV), which crystallises in colourless needles, m. p. 140°, gives a deep blue coloration with ferric chloride and is a moderately strong acid; it may be titrated with alkali hydroxide. According to Baeyer's tension hypothesis, the formation of this compound from the saturated ring compound involves an increase in the tension from 24·44° to 30° per valency. The ester is highly stable and resists the action of dilute acid or alkali for some time; with concentrated acid or alkali in the hot it gives resinous products, *as.*-diphenylsuccinic acid not being obtained. In the hot it gives with 50% sulphuric acid a cornflower blue coloration, and with the concentrated acid a cherry-red and then a green coloration, decomposition and formation of a brownish-black coloration finally taking place. Prolonged boiling with sodium ethoxide in alcoholic solution converts the ester into an *acid*, m. p. 125°, and reduction with platinum black and hydrogen yields mostly resinous products, a *compound*, m. p. 108°, being obtained in one instance. The ester instantly decolorises a solution of bromine in carbon disulphide, giving the *bromo*-derivative,

$$CO_2Et\cdot C\!\lessdot\!\begin{array}{l}CPh_2\\ C\cdot OBr\end{array},$$

which forms colourless crystals, m. p. 110°, and liberates iodine from potassium iodide solution.

Ethyl benzhydrylidene - ethyleneoxidecarboxylate [αβ - *oxido* - γγ-*diphenyl*-Δ^{β}-*butenoate*] (VII) forms colourless crystals, m. p. 124°. With about 50% sulphuric acid it gives a bright blue coloration, and with the concentrated acid yellow, red, violet, and brown colorations appear successively as the temperature rises. By chromic acid or by sodium dichromate in glacial acetic acid the ester is readily oxidised, yielding benzophenone; permanganate oxidises it only in the hot, whilst reducing agents, including platinum black, are without effect. The ester is not attacked by carbonyl

group reagents. Acetic anhydride converts the ester into the ester of benzhydrylidenepyruvic acid (see below), whilst the action of acetyl chloride yields the compound,

$$CPh_2{:}C(OH){\cdot}CH(OAc){\cdot}CO_2Et;$$

the latter then undergoes conversion into the β-*lactone*,

$$CPh_2{:}C{<}\genfrac{}{}{0pt}{}{O\overline{}}{CH(OAc)}{>}CO,$$

of β-*hydroxy*-α-*acetoxy*-γγ-*diphenyl*-Δ^{β}-*butenoic acid*, which forms colourless needles, m. p. 111°, and, when boiled with alkali hydroxide solution, is converted quantitatively into acetic acid and

Benzhydrylidenepyruvic acid (α-*keto*-γγ-*diphenyl*-Δ^{β}-*butenoic acid*), $CPh_2{:}CH{\cdot}CO{\cdot}CO_2H$; this acid, which may be obtained also by boiling ethyl αβ-oxido-γγ-diphenyl-Δ^{β}-butenoate with hydrochloric acid or potassium hydroxide solution, crystallises in white needles, m. p. 207°. In glacial acetic acid, sodium dichromate or hydrogen peroxide converts it into benzophenone. The *ethyl* ester, $C_{18}H_{16}O_3$, forms crystals, m. p. 110°.

Ethyl α-*bromo*-αβ-*oxido*-γγ-*diphenyl*-Δ^{β}-*butenoate*,

$$O{<}\genfrac{}{}{0pt}{}{C{:}CPh_2}{CBr{\cdot}CO_2Et},$$

obtained by the action of bromine on compound VII, forms colourless crystals, m. p. 117°, and is accompanied by the acid, m. p. 224° (see below), and by a small proportion of a neutral *compound*, m. p. 105—106°. When boiled for a short time with concentrated hydrochloric or hydrobromic acid, it is hydrolysed to β-*bromo*-α-*keto*-γγ-*diphenyl*-Δ^{β}-*butenoic acid*, $CPh_2{:}CBr{\cdot}CO{\cdot}CO_2H$, which forms colourless crystals, m. p. 224°, is readily converted into benzophenone by sodium dichromate in glacial acetic acid, and forms the *ethyl* ester, $C_{18}H_{15}O_3Br$, m. p. 162°.

As secondary products of the action of ethyl diazoacetate on diphenylketen the following were obtained: (1) an *acid*, m. p. 217°, which gives a deep blue coloration with ferric chloride, forms a sparingly soluble sodium salt, and is of complex composition; (2) a small proportion of a neutral *compound*, $C_{18}H_{16}O_3$, m. p. 158°, which is isomeric or polymeric with the principal products of the reaction.

The interaction of diphenylketen and methyl diazoacetate yields the corresponding *cyclo*propenol compound and *ethylene oxide* derivative, the latter, $C_{17}H_{14}O_3$, m. p. 145°, being isolated and analysed.

The action of diphenyldiazomethane on diphenylketen in ethereal solution yields the *compound*, $\genfrac{}{}{0pt}{}{N{\cdot}C({:}CPh_2)}{N\overline{}CPh_2}{>}O$, which forms yellow crystals, m. p. 136°, has the normal molecular weight in freezing benzene, and exhibits marked stability towards acids and alkalis. Nitrogen is eliminated when the compound is heated, but no definite products have been isolated.

From diphenylketen and diazomethane, a compound, possibly $CPh_2{:}C{<}\genfrac{}{}{0pt}{}{O}{CH_2}$, is obtained.

p-Methoxydiphenyldiazomethane and diphenylketen yield the *compound*, $\begin{matrix} N\text{———}C(:CPh_2) \\ \| \\ N\cdot CPh(C_6H_4\cdot OMe) \end{matrix}\!\!>\!O$ (?), which forms deep yellow crystals, m. p. 115—116°.

In absence of solvent and in an atmosphere of carbon dioxide benzoylphenyldiazomethane (1 mol.) and diphenylketen (2 mols.) react, yielding, as principal product, a neutral *compound*, $C_{42}H_{30}O_3N_2$, which forms crystals, m. p. 174°, but has not been investigated as regards constitution. T. H. P.

The Synthesis of *d*-3 : 4-Dihydroxyphenylalanine. KINSABURO HIRAI (*Biochem. Zeitsch.*, 1921, **114**, 67—70).—*Di*-(3-*acetoxy*-4-*methoxybenzylidene*)*glycine anhydride*,

$$C_4H_2O_2N_2[:CH\cdot C_6H_3(OMe)\cdot OAc]_2,$$

was prepared by heating glycine anhydride at 160—170° with vanillin, anhydrous sodium acetate, and acetic anhydride on the oil-bath for six and a half hours. Light yellow crystals were obtained, m. p. above 280°. dl-3 : 4-*Dihydroxyphenylalanine*, $C_6H_3(OH)_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, was prepared by boiling the condensation product with hydroiodic acid (D 1, 7) and red phosphorus under reflux for eight hours. It is crystalline and has m. p. 271—272° (decomp.). S. S. Z.

Constitution of Fluoranthene. Syntheses of *iso*Diphenic Acid and Fluorenone-1-carboxylic Acid. FRITZ MAYER and KARL FREITAG (*Ber.*, 1921, **54**, [*B*], 347—357).—The formula ascribed to fluoranthene by Fittig is based on its oxidation to fluoranthenequinone and then fluorenone-1-carboxylic acid; the latter acid can be converted into a diphenyldicarboxylic acid, which, on account of its degradation to *iso*phthalic acid, has been assumed to be diphenyl-2 : 3′-dicarboxylic acid (*iso*diphenic acid). Some uncertainty is, however, attached to the formulæ, since neither acid has been produced synthetically. This has now been effected, and Fittig's conclusions have received complete confirmation. The synthesis follows the line 2 : 3′-dimethylazobenzene → 4 : 4′-diamino-2 : 3′-dimethyldiphenyl → 2 : 3′-dimethyldiphenyl → diphenyl-2 : 3′-dicarboxylic acid.

2 : 3′-Azotoluene, b. p. 183—186°/12 mm., 185—187°/11 mm., is prepared from *m*-toluidine, *o*-nitrotoluene and sodium hydroxide at 200° (yield 12%), from *o*-toluidine, *m*-nitrotoluene and sodium hydroxide at 190—195° (yield 48%), or, preferably, by coupling diazotised *o*-toluidine with *o*-toluidine to 4′-amino-2 : 3′-dimethylazobenzene and de-amination of the latter with ethyl nitrite in alcoholic solution (yield 50—60%). It is simultaneously reduced and isomerised by stannous chloride and hydrochloric acid to 4 : 4′-diamino-2 : 3′-dimethyldiphenyl, amorphous, glassy mass, b. p. 243—246°/12 mm., which is characterised as a primary diamine by the preparation of a series of *azomethines* with benzaldehyde (m. p. 106—107°), salicylaldehyde (m. p. 160—161°), anisaldehyde

(m. p. 142—143°), *p*-chlorobenzaldehyde (m. p. 149—150°), *o*-chlorobenzaldehyde (m. p. 102—103°), and *p*-nitrobenzaldehyde (m. p. 195—196°). The *dibenzoyl* derivative has m. p. 245—246; the *tetra-acetyl* compound forms colourless leaflets, m. p. 191—192°, and is converted by short treatment with concentrated hydrochloric acid into the *di-acetyl* derivative, colourless, shining plates, m. p. 253—254°, which is also directly obtainable from the base. 4 : 4′-Diamino-2 : 3′-dimethyldiphenyl is transformed into the corresponding unstable *dihydrazino*-compound (*hydrochloride*, yellow needles), which is converted by copper acetate into 2 : 3′-dimethyldiphenyl, colourless, highly refractive oil, b. p. 273—274°, D^{22} 0·9984, n_D 1·5848. The hydrocarbon is oxidised by potassium permanganate to diphenyl-2 : 3′-dicarboxylic acid, colourless, interwoven needles, m. p. 215—216°, after previous softening (the *di-amide* forms long, colourless rods, m. p. 182—183°; the *di-anilide* has m. p. 219—220°). Concentrated sulphuric acid at 140—150° transforms diphenyl-2 : 3′-dicarboxylic acid into fluorenone-1-carboxylic acid, m. p. 192—194°, the yield, however, being only 12% of that theoretically possible.

In the synthesis just described, the 2 : 3′-position of the methyl groups is not definitely proved. It is, however, established in the following manner. A mixture of *o*- and *m*-iodotoluenes is heated with finely divided copper at 230—240°, thus yielding a mixture of 2 : 2′-, 2 : 3-′, and 3 : 3′-dimethyldiphenyls. The first of these can be removed by careful fractional distillation of the mixture, leaving the 2 : 3′- and 3 : 3′-isomerides, which are oxidised to the corresponding dicarboxylic acids; the latter can be separated by taking advantage of the fact that diphenyl-3 : 3′-dicarboxylic acid is practically insoluble in water, and the diphenyl-2 : 3′-dicarboxylic acid thus isolated is found to be identical with that obtained above. H. W.

Synthesis of Monobasic or Dibasic Acids by the Action of Malonic Acid on the Substituted Benzhydrols. Replacement of the Hydroxyl Group by the Carbomethoxy-group; $\cdot CH_2\cdot CO_2H$ or the Dicarbomethoxy-group; $\cdot CH(CO_2H)_2$. Léon Baillon (*Ann. Chim.*, 1921, **15**, 61—108).—Malonic acid reacts with the substituted *p*-methoxybenzhydrols at 100° to give derivatives of *iso*succinic acid. At higher temperatures substitued propionic acids are obtained (Fosse, A., 1907, i, 136). Thus *p*-methoxydiphenylcarbinol gives β-phenyl-β-*p*-methoxyphenyl*iso*succinic acid, $OMe\cdot C_6H_4\cdot CHPh\cdot CH(CO_2H)_2$, m. p. 178° (decomp.) (A., 1906, i, 975), giving *silver, sodium, calcium, barium, magnesium*, and *lead* salts. When heated at 180—200° it loses carbon dioxide and gives β-phenyl-β-*p*-methoxyphenylpropionic acid. *p*-Methoxyphenyl-*o*-tolylcarbinol, under similar conditions, gives β-p-*methoxyphenyl*-β-*o*-*tolyl*iso*succinic acid*, $OMe\cdot C_6H_4\cdot CH(C_6H_4Me)\cdot CH(CO_2H)_2$, m. p. 191° (decomp.), which gives *silver, sodium, calcium, barium, magnesium*, and *lead* salts, and on heating is decomposed, yielding β-p-*methoxyphenyl*-β-o-*tolylpropionic acid*, m. p. 101—102°, giving a *silver* salt.

p-Methoxyphenyl-*p*-tolylcarbinol yields β-p-*methoxyphenyl*-β-p-*tolyl*-iso*succinic acid*, m. p. 195° (decomp.), which gives *silver, sodium, calcium, barium, magnesium*, and *lead* salts, and is decomposed on heating to give β-p-*methoxyphenyl*-β-p-*tolylpropionic acid*, m. p. 140—142°, giving a *silver* salt. β-p-*Methoxyphenyl*-β-α-*naphthyl*iso*succinic acid*, m. p. 146° (decomp.), yields *silver, sodium, calcium, barium, magnesium* and *lead* salts, and on heating is decomposed, giving β-*p*-methoxyphenyl-β-α-naphthylpropionic acid, m. p. 116—117° (Fosse, *loc. cit.*).

The 3 : 4-dimethoxybenzhydrols behave in a similar manner to the *p*-methoxybenzhydrols. At 100° they react with malonic acid to give substituted *iso*succinic acids, but at 130—190° the product is a derivative of propionic acid. The following are described: β-*Phenyl*-β-3 : 4-*dimethoxyphenyl*iso*succinic acid*,

$$C_6H_3(OMe)_2\cdot CHPh\cdot CH(CO_2H)_2,$$

m. p. 165° (decomp.), giving *silver, sodium, calcium, barium, magnesium*, and *lead* salts. β-*Phenyl*-β-3 : 4-*dimethoxyphenylpropionic acid*, m. p. 109—111°, with its *silver* salt. β-3 : 4-*Dimethoxyphenyl*-β-o-*tolyl*iso*succinic acid*, m. p. 177° (decomp.), giving *silver, sodium, calcium, barium, magnesium*, and *lead* salts. β-3 : 4-*Dimethoxyphenyl*-β-o-*tolylpropionic acid*, m. p. 113—114°, with its *silver* salt. β-3 : 4-*Dimethoxyphenyl*-β-p-*tolyl*iso*succinic acid*, m. p. 185° (decomp.), with its *silver* salt. β-3 : 4-*Dimethoxyphenyl*-β-p-*tolylpropionic acid*, m. p. 135—136°. β-3 : 4-*Dimethoxyphenyl*-β-α-*naphthyl*iso*succinic acid*, m. p. 144° (decomp.). β-3 : 4-*Dimethoxyphenyl*-β-α-*naphthylpropionic acid*, m. p. 147—148°.

Similar results were obtained with 3 : 4-methylenedioxy-derivatives of benzhydrol. The following compounds are described: β-3 : 4-*Methylenedioxyphenyl*-β-o-*tolyl*iso*succinic acid*, m. p. 183° (decomp.). β-3 : 4-*Methylenedioxyphenyl*-β-o-*tolylpropionic acid*, m. p. 145—147°. β-3 : 4-*Methylenedioxyphenyl*-β-p-*tolyl*iso*succinic acid*, m. p. 180° (decomp.). β-3 : 4-Methylenedioxyphenyl-β-*p*-tolylpropionic acid, m. p. 161°. β-3 : 4-*Methylenedioxyphenyl*-β-α-*naphthyl*iso*succinic acid*, m. p. 185° (decomp.), and β-3 : 4-methylenedioxyphenyl-β-α-naphthylpropionic acid, m. p. 205—206°.

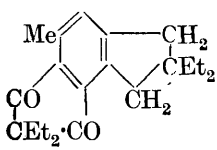
The substituted *p*-dimethylaminobenzhydrols react similarly, and the following compounds are described: β-*Phenyl*-β-p-*dimethylaminophenyl*iso*succinic acid*, m. p. 124° (decomp.), with its *silver* salt. β-Phenyl-β-*p*-dimethylaminopropionic acid, m. p. 184—185°, *silver* salt. β-p-*Dimethylaminophenyl*-β-o-*tolyl*iso*succinic acid*, m. p. 183° (decomp.), with its *silver* salt. β-p-*Dimethylaminophenyl*-β-o-*tolylpropionic acid*, m. p. 158—160°, with its *silver* salt. β-p-*Dimethylaminophenyl*-β-p-*tolyl*iso*succinic acid*, m. p. 193° (decomp.), with its *silver* salt. β-p-*Dimethylaminophenyl*-β-p-*tolylpropionic acid*, m. p. 173—175°, with its *silver* salt. β-p-*Dimethylaminophenyl*-β-α-*naphthyl*iso*succinic acid*, m. p. 172° (decomp.), with its *silver* salt. β-*p*-Dimethylaminophenyl-β-α-naphthylpropionic acid. β-p-*Dimethylaminophenyl*-β-p-*nitrophenylpropionic acid*, m. p. 179—180°, giving a *silver* salt, a *methyl* ester, m. p. 91—92°, with its *platinichloride*, and an *ethyl* ester with its *platinichloride*. β-p-*Dimethylaminophenyl*-β-m-*nitrophenylpropionic acid*, m. p. 143—145°, giving

a *silver* salt, a *methyl* ester with its *platinichloride*, and an *ethyl* ester, m. p. 67—68°, with its *platinichloride*. W. G.

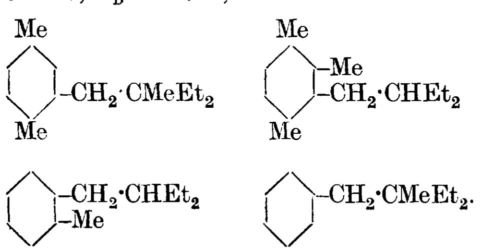
Synthesis of Indanediones. VII. KARL FLEISCHER (*Annalen*, 1921, **422**, 231—265. Compare A., 1917, i, 572).—[With WALTER WOLFGANG MELBER].—Condensation of toluene with diethylmalonyl chloride yields, as would be expected: (1) 5-*Methyl*-2 : 2-*diethylindane*-1 : 3-*dione*, $CEt_2<{CO \atop CO}>C_6H_3Me$, which crystallises in stout crystals, m. p. 49—50°, and, when oxidised by means of nitric acid under pressure, gives, first, 2 : 2-*diethylindane*-1 : 3-*dione*-5-*carboxylic acid*, $C_{14}H_{14}O_4$, m. p. 136—137°, and then benzene-1 : 2 : 4-tricarboxylic (trimellitic) acid. (2) 4-*Methyl*-2 : 2-*diethylindane*-1 : 3-*dione*, $C_{14}H_{16}O_2$, which is a pale yellow, oily liquid, b. p. 150°/14 mm., and, on oxidation by means of nitric acid under pressure, yields *iso*phthalic acid; the latter is doubtless formed from the intermediate product, hemimellitic (benzene-1 : 2 : 3-tricarboxylic) acid by loss of carbon dioxide. (3) $\gamma\gamma$-*Di*-p-*toluoylpentane*, $CEt_2(CO{\cdot}C_6H_4Me)_2$, which forms white, glistening crystals, m. p. 94—95°, does not react with phenylhydrazine or hydroxylamine, and gives *p*-toluic acid when treated with potassium hydroxide solution.

When nitrated, 5-methyl-2 : 2-diethylindane-1 : 3-dione yields the *compound*, $C_{14}H_{15}O_4N$, m. p. 82—83° with previous softening, and the 4-methyl isomeride a small proportion of a crystalline *compound*, m. p. 185° with previous softening.

Reduction of 5-methyl-2 : 2-diethylindane-1 : 3-dione by means of zinc amalgam and excess of fuming hydrochloric acid (compare Clemmensen, A., 1913, i, 733) yields 5-*methyl*-2 : 2-*diethylhydrindene*, $CEt_2<{CH_2 \atop CH_2}>C_6H_3Me$, which is a colourless, mobile oil, b. p. 123—127°/12 mm., $D^{21 \cdot 5}$ 0·9197, n_D 1·51055, and condenses with diethylmalonyl chloride, giving 5-*methyl*-2 : 2 : 7 : 7-*tetra-ethyl-v-dihydrindane*-6 : 8-*dione* (annexed formula) as a brown oil, b. p. 212—221°/15 mm.



Similar reduction of 4-methyl-2 : 2-diethylindane-1 : 3-dione yields a colourless, oily *compound*, b. p. 110—116°/12 mm., D^{22} 0·9007, n_D 1·50742, which has one of the four annexed formulæ.

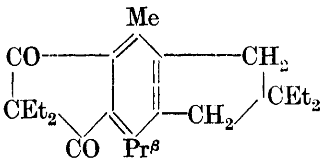


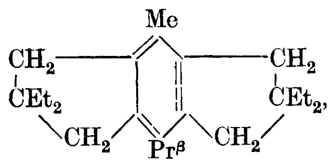
The condensation of *p*-cymene and diethylmalonyl chloride (compare Freund and Fleischer, A., 1910, i, 490) has been carried out under modified conditions and an improved yield of 4-methyl-2 : 2-diethyl-7-*iso*propylindane-1 : 3-dione, m. p. 37—38·5° obtained. This compound, which

is accompanied by a small proportion of impurity very difficult to separate, gives benzene-1 : 2 : 3 : 4-tetracarboxylic acid on oxidation with nitric acid, whilst on reduction by means of amalgamated zinc and fuming hydrochloric acid it yields *4-methyl-2 : 2-diethyl-7-*iso*propylhydrindene*,

$$\mathrm{CEt_2}{<}{}^{\mathrm{CH_2}}_{\mathrm{CH_2}}{>}\mathrm{C_6H_2MePr^{\beta}}$$

as a colourless liquid, b. p. 157—165°/15 mm., D^{22} 0·9148, n_D 1·5112. Condensation of the latter with diethylmalonyl chloride gives *4-methyl-2 : 2 : 6 : 6-tetraethyl-8-*iso*propyl-s-dihydrindane-5 : 7-dione* (annexed formula), b. p. 238—242°/20 mm., which, on oxidation by means of nitric acid, yields mellitic acid and a small proportion of another acid, probably *2 : 2-diethylindane-1 : 3-dione-4 : 5 : 6 : 7-tetracarboxylic acid*, and on reduction by means of amalgamated zinc and fuming hydrochloric acid is converted into *4-methyl-2 : 2 : 6 : 6-tetraethyl-8-*iso*propyl-s-dihydrindene* (annexed formula), forming drusy masses of colourless, lanceolate crystals, m. p. 69—71°, b. p. 215—220°/12 mm., D^{22} (liquid) 0·9466, n_D 1·5247.





Condensation of 4-methyl-2 : 2-diethyl-7-*iso*propylhydrindene with acetyl chloride in presence of aluminium chloride gives an oily *compound*, $C_{19}H_{28}O$, b. p. 190—195°/14 mm., which is apparently 5 (or 6)-*acetyl-4-methyl-2 : 2-diethyl-7-*iso*propylhydrindene.*

The action on naphthalene of diethyl- or dimethyl-malonyl chloride yields in each case the three expected naphthindandiones, the constitutions of which have been determined (A., 1910, i, 490; 1913, i, 1073; 1914, i, 48). Condensation of α-methylnaphthalene with diethylmalonyl chloride yields an oil, b. p. 234—236°/14 mm., which has the composition of an *α-methyldiethylnaphthindanedione* and is probably a mixture of isomerides; oxidation of this oil by means of fuming nitric acid under pressure gives a white, crystalline substance which softens at 210°, decomposes at 223—226°, and has approximately the composition of benzenepentacarboxylic acid. Condensation of β-methylnaphthalene with diethylmalonyl chloride yields a viscous yellow oil, b. p. 233—239°/15 mm., which has the composition of *β-methyldiethylnaphthindanedione*, $C_{18}H_{18}O_2$, and, after the lapse of a year, deposits crystals, m. p. 79—82°, of the same composition.

[With JOHANN STEMMER].—Further investigations have also been made on the condensation of dimethylmalonyl chloride with phenolic ethers. The action of dimethylmalonyl chloride on quinol dimethyl ether yields: (1) *4 : 7-Dimethoxy-2 : 2-dimethylindane-1 : 3-*

dione, $CMe_2<{CO \atop CO}>C_6H_2(OMe)_2$, which is a white compound, m. p. 170—171°, with previous softening, and dissolves in concentrated sulphuric acid, giving a brownish-green coloration. (2) 1-iso*Butyryl-5-hydroxy-2-methoxybenzene* or 1-iso*butyryl-6-hydroxy-3-methoxybenzene*, $C_{11}H_{14}O_3$, which is an oily liquid, b. p. 163°/25 mm., of phenolic properties. (3) A small proportion of 4-*hydroxy-7-methoxy-2:2-dimethylindane-1:3-dione*, $CMe_2<{CO \atop CO}>C_6H_2(OH)\cdot OMe$, which is a white compound, m. p. 132—134°; in alkaline solution it shows marked fluorescence, and it dissolves in concentrated sulphuric acid, giving a brownish-green solution.

With catechol dimethyl ether, dimethylmalonyl chloride condenses, forming: (1) (? ?)-*Dimethoxy-2:2-dimethylindane-1:3-dione*,

$$CMe_2<{CO \atop CO}>C_6H_2(OMe)_2,$$

which crystallises in long, white threads, m. p. 228°, and is hydrolysed to dihydroxydimethylindanedione (see below) when boiled with hydriodic acid (D 1·72). (2) (?)-*Hydroxy-(?)-methoxy-2:2-dimethylindane-1:3-dione*,

$$CMe_2<{CO \atop CO}>C_6H_2(OH)\cdot OMe,$$

which separates in lanceolate crystals, m. p. 192°, with previous softening, exhibits slight yellow fluorescence in dilute alkaline solution, gives a pale yellow solution in concentrated sulphuric acid, and, when boiled with hydriodic acid, yields (3) (?)-*Dihydroxy-2:2-dimethylindane-1:3-dione*, $CMe_2<{CO \atop CO}>C_6H_2(OH)_2$, which crystallises in small leaflets, m. p. 297°, exhibits brown fluorescence in alkaline solution, and gives a pale yellow solution in concentrated sulphuric acid. In these three compounds the indanedione ring evidently occupies the same position, but it is not known if the methoxy- or hydroxy-groups are arranged vicinally or symmetrically.

Hydroxyacetoxydimethylindandione, $C_{14}H_{14}O_5$, crystallises in short, white needles, m. p. 176—177°, and *diacetoxydimethylindanedione*, $C_{15}H_{14}O_6$, in white needles, m. p. 152°.

As was formerly found with diethylmalonyl chloride (A., 1915, i, 971), so also with dimethylmalonyl chloride, the reaction with resorcinol dimethyl ether proceeds abnormally, the products consisting principally of dimethylmalonic acid, together with a small proportion of an oil.

Further, from dimethylmalonyl chloride and anisole, no indandione derivative has yet been obtained, the products consisting of: (1) A neutral *compound*, $C_{18}H_{18}O_4$, which forms an oil, b. p. 150—160°/19 mm. and gives a reddish-brown solution in concentrated sulphuric acid; its constitution is possibly,

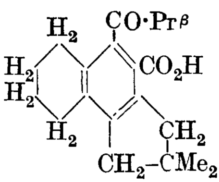
$$OMe\cdot C_6H_4\cdot CO\cdot CMe_2\cdot CO\cdot OPh,$$

although it does not yield an acid, but remains unchanged, when boiled with alkali. (2) An iso*butyrylphenol*, $OH\cdot C_6H_4\cdot CO\cdot CHMe_2$, b. p. 125—135°/20 mm., which was obtained in insufficient amount to allow its constitution to be fixed.

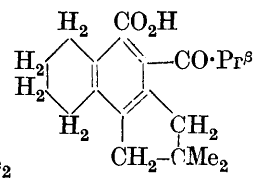
In general, diethylmalonyl chloride is far more suitable for preparing indandione derivatives from phenolic ethers than is dimethylmalonyl chloride, which exhibits a marked tendency to act as a substituted acetyl chloride. T. H. P.

Synthesis of Indanediones. IX. Action of Substituted Malonyl Chlorides on Partly Hydrated Aromatic Hydrocarbons. KARL FLEISCHER and FRITZ SEIFERT (*Annalen*, 1921, **422**, 272—317).—Nearly the whole of the work here described has been already published in condensed form (A., 1920, i, 620), the new matter being as follows.

When boiled with aqueous potassium hydroxide, 2 : 2 : 5 : 5-tetramethyltetrahydronaphthdihydrindane-4 : 6-dione (*loc. cit.*) yields an acid, which crystallises in bundles of microscopic needles, m. p. 181°, with previous softening and is either 2 : 2-*dimethyltetrahydronaphth*-αβ-*hydrindene*-4-iso*butyryl*-5-*carboxylic acid* (I) or the isomeric -5-iso*butyryl*-4-*carboxylic acid* (II); this acid does not react with phenylhydrazine.



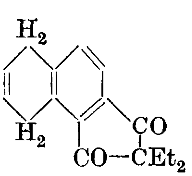
(I.)

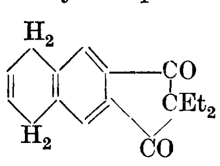


(II.)

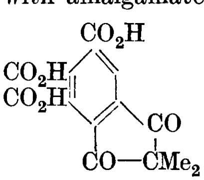
The acid, m. p. 134—135°, obtained by hydrolysis of 2 : 2-diethyltetraphydronaphth-αβ-indane-1 : 3-dione (*loc. cit.*), is 1-*diethylacetyltetrahydronaphthalene-2-carboxylic acid*, $C_{17}H_{22}O_3$.

Condensation of dihydronaphthalene with diethylmalonyl chloride yields a *diethyldihydronaphthindanedione*, $C_{17}H_{18}O_2$, which crystallises in rosettes of needles, m. p. 99—101°, and has one of the two annexed formulæ.



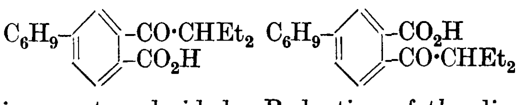


Condensation of tetrahydroacenaphthene with dimethylmalonyl chloride yields 2 : 2-*dimethyltetrahydroacenaphth*-αβ-*indane*-1 : 3-*dione*, $C_{17}H_{18}O_2$, m. p. 105—106°, which gives 2 : 2-*dimethyltetrahydroacenaphth*-αβ-*hydrindene*, $C_{17}H_{22}$, b. p. 173—175°/13 mm., D^{22} 0·9884, n_D 1·5399, when reduced with amalgamated zinc and hydrochloric acid, and 2 : 2-*dimethylindane*-1 : 3-*dione*-5 : 6 : 7-*tricarboxylic acid* (annexed formula), m. p. 245°, when oxidised with nitric acid.



Oxidation of 2 : 2-diethyltetrahydroacenaphth-αβ-indane-1 : 3-dione yields a mixture of benzenepentacarboxylic acid and 2 : 2-*diethylindane*-1 : 3-*dione*-5 : 6 : 7-*tricarboxylic acid* (*loc. cit.*), $C_{16}H_{14}O_8$, which sinters at 180°, m. p. 188—190° (decomp.).

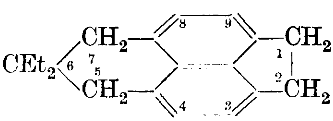
Condensation of diethylmalonyl chloride with tetrahydrodiphenyl yields 5-cyclo*hexyl*-2 : 2-*diethylindane*-1 : 3-*dione*, $C_{19}H_{22}O_2$, m. p. 88°, which on oxidation gives trimellitic acid with intermediate formation of 2 : 2-diethylindane-1 : 3-dione-5-carboxylic acid (compare Fleischer, preceding abstract) and also a small proportion of a compound, m. p. 184—186°, which sublimes. When boiled with potassium hydroxide solution (1 : 1), the dione yields two isomeric compounds, which are termed α- and β-1-(or 2)-α-*ethylbutyryl*-5-cyclo*hexylbenzene*-2 (or 1)-*carboxylic acids* (annexed formulæ); these have m. p. 198° and 98—100°, but which is which is as yet undecided. Reduction of the dione by means of amalgamated zinc and hydrochloric acid yields 5-cyclo*hexyl*-2:2-*diethylhydrindene*, $C_{19}H_{26}$, as a colourless oil, b. p. 220°/27 mm., D^{20} 0·9475, n_D 1·5274.



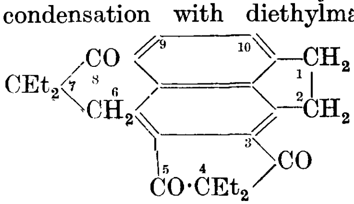
T. H. P.

Synthesis of Indanediones. X. Pericyclic Derivatives of Acenaphthene. KARL FLEISCHER and FRITZ SIEFERT (*Annalen*, 1921, **422**, 317—325).—Few compounds with a hydrocarbon ring in the peri-position of acenaphthene are known and have been obtained almost exclusively by the indanedione synthesis, but no hydrocarbon of this type has yet been prepared; the authors find that such a hydrocarbon may be prepared by means of the method used (compare preceding abstracts) to convert indanediones into their fundamental hydrocarbons.

Reduction of diethyl*peri*acenaphthindandione cannot be effected by Clemmensen's method, but when carried out by means of phosphorus and hydriodic acid under pressure, the resulting product is 6 : 6-*diethyl*peri*acenaphthindane* (annexed formula), which forms lanceolate crystals or step-like aggregates of hexagonal plates, m. p. 93—95°. This method of preparing the hydrocarbon is, however, unsatisfactory, since the aromatic nucleus is always attacked and an oily product formed. At the ordinary pressure the reduction proceeds in stages, giving: (1) 7-*Keto*-6 : 6-*diethyl*peri*acenaphthindane*, $C_{19}H_{20}O$, which forms yellow crystals and in concentrated sulphuric acid gives a bright red solution showing green fluorescence; (2) 6 : 6-diethyl*peri*acenaphthindane.



The monoketone, 7-keto-6 : 6 : diethyl*peri*acenaphthindane, exhibits the character of a hydrocarbon in so far that it undergoes condensation with diethylmalonyl chloride, giving 4 : 4 : 7 : 7-*tetraethyl*-ββ-peri*acenaphthdi-indane*-3 : 5 : 8-*trione* (annexed formula), which crystallises in brown, microscopic, rhombic plates, m. p. 146—147°, and dissolves in concentrated sulphuric acid to a yellowish-red solution exhibiting green fluorescence.

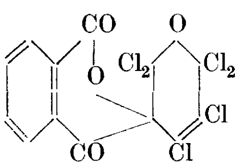


Reduction of this triketone by means of phosphorus and hydriodic acid gives the *compound*, $C_{26}H_{30}O_2$, which crystallises in yellowish-white, pointed plates, m. p. 112°, and dissolves in concentrated sulphuric acid, giving a bright red solution showing brown fluorescence. Since 6 : 6-diethyl*peri*acenaphthindane condenses with diethylmalonyl chloride, giving 4 : 4 : 7 : 7-*tetraethyl*-ββ-peri*acenaphthdi-indane*-3 : 5-*dione*, $C_{26}H_{30}O_2$, which crystallises in long, pale yellow, pointed plates, m. p. 93—94°, and dissolves in concentrated sulphuric acid to a bright red solution, and since also the keto-group in the 3-position of the triketone molecule is less protected and more readily accessible to reduction than that in the 5-position, the conclusion is drawn that the compound, m. p. 112°, is 4 : 4 : 7 : 7-*tetraethyl*-ββ-peri*acenaphthdi-indane*-5 : 8-*dione*. T. H. P.

Degradation Reactions in the Anthraquinone Series. K. Fries and W. Hartmann (*Ber.*, 1921, **54**, [*B*], 193—200. Compare Fries and Auffenberg, A., 1920, i, 236).—1 : 1 : 3 : 4 : 4-*Pentachloro-2-keto*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*,

$$C_6H_4<\begin{array}{l}CO\cdot C\cdot CCl_2\cdot CO\\ CO\cdot C\cdot CCl_2\cdot CHCl\end{array},$$

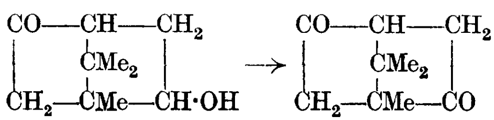
shining yellow leaflets, m. p. 213°, is obtained by the exhaustive chlorination of β-aminoanthraquinone suspended in glacial acetic and fuming hydrochloric acids at the laboratory temperature; it is reduced by stannous chloride to 1 : 3-*dichloro-2-hydroxyanthraquinone*, yellow needles, m. p. 208° (*acetate*, small yellow needles, m. p. 179°) and is transformed by sodium acetate in boiling glacial acetic acid solution into 1 : 3 : 4-*trichloro-2-hydroxyanthraquinone*, yellow needles, m. p. 252°, which yields sparingly soluble, red *salts* with the alkali metals and an *acetate*, yellow needles or leaflets, m. p. 174°. In the latter respect, the substance differs from the isomeric 2 : 2 : 3 : 4 : 4-pentachloro-1-keto-1 : 2 : 3 : 4-tetrahydroanthraquinone which, in these circumstances, is transformed into *o*-2 : 3 : 4 : 6-tetrachloro-5-hydroxybenzoylbenzoic acid and the present reaction must be ascribed to a simultaneous reduction and elimination of hypochlorous acid such as is not infrequently observed with hydroaromatic ketoketonic chlorides. An attempt to avoid the reduction by allowing sodium acetate to react with 2 : 2 : 3 : 4 : 4-pentachloro-1-keto-1 : 2 : 3 : 4-tetrahydroanthraquinone in the presence of an excess of chlorine led to an unexpected result, the product being a *substance* (annexed formula), colourless rhombohedra, m. p. 151—152°, which is reduced by stannous chloride and glacial acetic acid to *o*-2 : 3 : 4 : 6-tetrachloro-5-hydroxybenzoylbenzoic acid, m. p. 277°. The lactonic nature of the substance is deduced from the fact that it dissolves in aqueous-alcoholic sodium hydroxide solution and, on addition of a mineral acid, gives *o*-2 : 2 : 3 : 4 : 6 : 6-*hexachloro*-1-*keto*-5-*hydroxy*-



benzoylbenzoic acid, needles or coarse prisms, m. p. 204° (decomp.), which is readily re-converted into the lactone by acetic anhydride in the presence of a few drops of concentrated sulphuric acid. The hydroxy-acid is reduced by stannous chloride in glacial acetic acid solution to phthalic acid and tetrachlororesorcinol, long needles, m. p. 140° (diacetate, m. p. 144°). H. W.

The Catalytic Action of Mercury in the Sulphonation of Anthraquinone. (MLLE) A. ROUX and JH. MARTINET (*Compt. rend.*, 1921, **172**, 385—387).—When anthraquinone is sulphonated by heating with sulphuric acid alone it is the 2-sulphonic acid which is obtained, but in the presence of mercury at a lower temperature the 1-sulphonic acid is the product. The explanation proposed is that in all cases it is the 1-sulphonic acid which is first formed, but that in the sulphonation with sulphuric acid the temperature is such that the velocity of transformation of the 1- into the 2-acid is as great as the velocity of sulphonation. With mercury present as a catalyst, the sulphonation takes place at a lower temperature, and thus the velocity of sulphonation is more rapid than that of transformation. This is confirmed by the fact that the 1-sulphonic acid is readily converted into the 2-acid by heating with sulphuric acid at 180°, and further by the fact that if the sulphonation in the presence of mercury is carried out at 160° the 2-acid is the product. W. G.

***p*-Diketocamphane and the Constitution of Schrötter's Oxycamphor.** J. BREDT and AUG. GOEB (*J. pr. Chem.*, 1920, [ii], **101**, 273—292).—Acetoxycamphor, originally obtained by Schrötter (A., 1882, 66) by oxidation of a mixture of bornyl and *iso*bornyl acetates, has m. p. 77° (*semicarbazone*, $C_{17}H_{21}O_3N_3$, needles, m. p. 248°, decomp.), and cannot be obtained from *iso*-bornyl acetate, being produced from the bornyl derivative. Hydroxycamphor, m. p. 238—246° (compare Schrötter), is a mixture of two stereoisomerides, of which the *exo*-form, m. p. 237·5—238°, corresponding with borneol, is obtained by treatment with zinc chloride; the *phenylurethane*, needles, m. p. *ca.* 110°; *semicarbazone*, $C_{11}H_{19}O_2N_3$, needles, m. p. 222—224° (decomp.), is converted into borneol when heated with sodium ethoxide. Oxalic acid was the sole recognisable product of the action of nitric acid on the hydroxy-compound (compare Schrötter), which is distinct from the isomerides prepared by Manasse and Schmiedeberg, since it is oxidised by chromic acid to "*paradiketocamphane*," m. p. 206·5—207°, in which the optical activity is preserved ($\alpha_D^{13.5}$ + 103·42°). This would not be the case if both carbonyl groups were attached to the same bridge carbon atom, and the two compounds are therefore represented by the annexed formulæ. *Paradiketocamphane disemicarbazone*, $C_{12}H_{20}O_2N_6$, m. p. above 262°, is converted into camphane by Wolff's method of reduction with sodium



ethoxide. *Paradihydroxycamphane*, $C_{10}H_{18}O_2$, from hydroxycamphor and sodium, is a sticky mass (*diacetate*, $C_{14}H_{22}O_4$, b. p. 151·5°/15 mm). The *compound*, $C_{20}H_{30}O_5S$, m. p. 187° (*semicarbazone*, m. p. *ca.* 200°) is produced by the action of thionyl chloride on hydroxycamphor, whilst a product free from halogen, but containing phosphorus, results when phosphorus pentachloride is employed. J. K.

Preparation of Limonene and Pinene Nitrosochlorides. H. RUPE (*Helv. Chim. Acta*, 1921, **4**, 149—150).—The following method, worked out by the author in conjunction with KARL LÖFFL, gives a 90% yield of either limonene or pinene nitrosochloride. On to a thin paste of sodium chloride and crude hydrochloric acid contained in a pump flask, crude concentrated sulphuric acid (about 2 parts) and moderately concentrated sodium nitrate (about 3 parts) are dropped from two dropping-funnels, excess of hydrochloric acid being avoided. The mixed gases are passed first through an empty washing bottle, then through one charged with calcium chloride, both in ice, and finally into a cylinder containing a solution of limonene or pinene in its own volume of ether and one-half of its volume of glacial acetic acid, this being well cooled in ice and salt. The colour of the solution is at first pale green and changes to bluish-green, a brown tint indicating excess of nitrous gases and dark green excess of hydrogen chloride; in the latter case, practically no solid nitrosochloride is obtained.
T. H. P.

Action of Hydracids on Essential Oil of *Juniperus oxycedrus*. Hydrochloride, Hydrobromide, and Hydriodide of Cadinine. R. HUERRE (*J. Pharm. Chim.*, 1921, [vii], **23**, 81—89; *J. Soc. Chim. Biol.*, 1921, **2**, 239—246).—The essential oil of *Juniperus oxycedrus* on treatment with hydrogen chloride, hydrogen bromide, and hydrogen iodide gives crystalline products consisting entirely of the dihydrochloride, m. p. 116°, $[\alpha]_D$ − 36·43°, dihydrobromide, m. p. 125°, $[\alpha]_D$ − 36·50°, and dihydriodide, m. p. 106°, $[\alpha]_D$ − 47·56°, of lævorotatory cadinene respectively, identical with the corresponding compounds obtained from oil of cade. The reactions are carried out either by the action of the dry gaseous acid on an ethereal solution of the oil, or on an alcoholic solution of the oil, or by the action of a saturated solution of the gas in glacial acetic acid on the oil. Of these methods the latter in all cases gave the best results, and of the three compounds the dihydriodide was obtained in by far the best yield. Calculated on the amount of dihydriodide obtained, the content of cadinene in the oil varied with different samples between 21·1% and 30·6%.
G. F. M.

Perilla Oil and Chamæcyparis (Japanese Cedar) Oil. YÔSHICHI NISHIZAWA (*J. Tokyo Chem. Soc.*, 1920, **41**, 1039—1042).—Limonene was isolated from the fraction b. p. 45—50°/

11 mm. of perilla oil; and pinene from the fraction, b. p. 156—157°, of Japanese cedar oil. K. K.

A Reaction of American Wormseed Oil. ALFONS LANGER (*Pharm. Zeit.*, 1921, **66**, 191).—When American wormseed oil (*Chenopodium ambrosioides*) is heated with phenolphthalein in the presence of toluene, reaction occurs, and at about 175° a clear mass is obtained; after terpenes and the toluene have been removed by distillation with steam, the mass is treated with dry toluene in which the reaction product dissolves, leaving any excess of phenolphthalein insoluble. The product is a reddish-yellow resin which is readily soluble in chloroform, ether, alcohol, warm toluene, or alkali solutions; from the latter it is precipitated, on the addition of acids, in the form of a yellow powder which melts below 100° to give a reddish-yellow resin. W. P. S.

The Microchemistry of Chitosan Compounds. HERMANN BRUNSWIK (*Biochem. Zeitsch.*, 1921, **113**, 111—124).—Utilising van Wisselingh's micro-method, the author reinvestigated the chemical properties of chitosan. Identical chitosan sphaerocrystals were obtained in various plant- and animal-tissues, and it is concluded that the chitosan in all cases is therefore also identical. "Lycoperdin" is a degradation product of chitosan.

S. S. Z.

Glucosides. VIII. Glycyrrhizin. P. KARRER, W. KARRER, and J. C. CHAO (*Helv. Chim. Acta*, 1921, **4**, 100—112. Compare A., 1920, i, 857).—Glycyrrhizic acid has been isolated from *Glycyrrhiza glabra* by way of its potassium salt (compare Tschirch and Cederberg (A., 1907, i, 545), the precautions recommended by Tschirch and Gauchmann (A., 1908, i, 898) being found unnecessary. The acid is free from nitrogen, but, like its potassium salt and its sugar-free component, glycyrrhetic acid, it yields methane when heated; as this gas is difficult of combustion, it has probably been mistaken for nitrogen by various earlier investigators, who apparently used the Dumas method of estimating nitrogen. This formation of methane probably explains also the low values for the percentages of carbon and hydrogen in glycyrrhetic acid and its allies obtained by Tschirch and Cederberg (*loc. cit.*).

Glycyrrhetic acid, prepared by hydrolysing potassium glycyrrhizate by means of about 1% sulphuric acid solution in an autoclave, crystallises in drusy aggregates of long, white needles, m. p. 297—298° (Tschirch and Cederberg, *loc. cit.*, gave m. p. about 90° lower), and contains 76·23% C. and 10·23% H. (Tschirch and Cederberg gave 70·53% C. and 8·89% H.); these figures indicate the formula $C_{45}H_{72}O_6$ or possibly $C_{44}H_{70}O_6$. In alcohol, the molecular weight is far smaller than the calculated value, evidently owing to dissociation. The *acetyl* derivative, $C_{45}H_{70}O_6Ac_2$, forms crystals. The *methyl* ester, $C_{46}H_{74}O_6$, obtained from the acid and diazomethane in ethereal solution, forms white needles, m. p. 241°,

and has the normal molecular weight in boiling alcohol. The *ethyl* ester, similarly obtained, crystallises in needles, m. p. 246—248°.

Deoxyglycyrrhetin, $C_{45}H_{72}O_5$, obtained by heating potassium glycyrrhetate with concentrated hydriodic acid and phosphonium iodide, crystallises in white leaflets, m. p. about 298—300° (uncorr.), and is insoluble in sodium hydroxide solution, even in the hot. Its *acetyl* derivative, $C_{45}H_{70}O_5Ac_2$, forms microscopic needles and begins to decompose at 260°.

Hydrolysis of potassium glycyrrhizate yields glycyrrhetic acid (1 mol.) and glycuronic acid lactone (2 mols.), but comparison of the formulæ of the initial and final products indicates the hydrolysis to be a complicated one. Tschirch and his collaborators regard glycyrrhetic acid as a substituted dihydroxynaphthalene, but this cannot be the case, since the esters of this acid are insoluble in sodium hydroxide solution; the two hydroxyl groups must, indeed, be alcoholic and not phenolic in character. Since partial oxidation or other similar method of degradation, when applied to glycyrrhetic acid, yields no well-defined products, the authors consider it probable that the carbon skeleton of this acid has a complicated aliphatic or hydroaromatic character; the traces of naphthalene obtained by distilling glycyrrhizin with zinc dust, and the small properties of phthalic acid formed on oxidation of the glucoside (Tschirch and Gauchmann, A., 1909, i, 318) presumably arise from pyrogenic condensations. The authors find that distillation of glycyrrhizic acid with zinc dust or its decomposition in a vacuum yields oils poor in oxygen and similar to colophony, but no individual products could be isolated from these oils. T. H. P.

Glucosides. IX. P. KARRER, ROSA BAUMGARTEN, S. GÜNTHER, W. HARDER and LINA LANG (*Helv. Chim. Acta*, 1921, **4**, 130—148).—In earlier papers (A., 1917, i, 539; A., 1919, i, 338, 594; A., 1920, i, 370, 395, 857) it has been shown that glucosides of α- or ortho-hydroxycarboxylic acids and of ortho-aminocarboxylic acids may be prepared by treating the silver salts of such acids with acetobromoglucose, the acetylated glucoside and the glucose ester of the acid being formed simultaneously. If the silver is really connected with the hydroxyl group by a secondary valency, the action of acetobromoglucose on silver *m*- and *p*-hydroxybenzoates should yield no glucoside; this is actually the case, the sole products of these reactions being the tetra-acetylglucose esters of the acids. With silver thiolacetate, the formation of the thioglucoside would be expected, owing to the stable linking of the silver with the sulphur; this linking is found, indeed, to be so stable that no reaction occurs with acetobromoglucose. The ethyl tetra-acetylglucosidothiolacetate may, however, be prepared by treating ethyl sodiothiolacetate, $CO_2Et \cdot CH_2 \cdot SNa$, with acetobromoglucose (compare Schneider, Sepp, and Stiehler, A., 1918, i, 252), and yields the thiolacetic acid glucoside on hydrolysis.

Certain other glucosides similar to the natural primeverin and

primulaverin (Karrer and Weidmann, A., 1920, i, 395) have also been prepared by the method described above. Thus, from silver 1-hydroxy-5-methoxybenzoate, β-tetra-acetyl-*d*-glucosido-2-hydroxy-5-methoxybenzoic acid and the tetra-acetylglucose ester of 5-methoxy-2-hydroxybenzoic acid were obtained; the former of these products may be converted into β-*d*-glucosido-2-hydroxy-5-methoxybenzoic acid and this, by means of diazomethane, into the corresponding methyl ester, which differs from primulaverin only in the nature of the sugar residue. Like β-*d*-glucosidosalicylic acid and β-*d*-glucosido-4-methoxysalicylic acid, β-*d*-glucosido-2-hydroxy-5-methoxybenzoic acid is a comparatively stable compound; this is noteworthy, since the methods previously used for synthesising glucosides are inapplicable to the construction of glucosides of ortho-hydroxycarboxylic acids.

Silver gentisate and acetobromoglucose readily react in toluene solution, but the only product obtainable is the tetra-acetyl-*d*-glucose ester of gentisic acid. Similarly, silver orsellinate gives only the tetra-acetyl-*d*-glucose ester of the acid.

It has been found previously (A., 1919, i, 594) that the silver salt of inactive mandelic acid and acetobromoglucose react, yielding the tetra-acetylglucoside and the tetra-acetylglucose ester of mandelic acid, together with the compound,

$$C_6H_7O_5Ac_4{\cdot}O{\cdot}CHPh{\cdot}CO_2{\cdot}C_6H_7O_5Ac_4,$$

which is both glucoside and ester. In this reaction only the *l*-mandelic acid is able to take up the two sugar residues, so that the inactive mandelate yields only the tetra-acetyl-*d*-glucose ester of β-tetra-acetyl-*d*-glucosido-*l*-mandelic acid, an asymmetric synthesis of mandelic acid being thus effected chemically. A similar phenomenon is observed with simple derivatives of mandelic acid. Thus, the silver salts of (1) inactive *o*-chloro- and (2) inactive *p*-methyl-mandelic acids give rise only to (1) β-tetra-acetyl-*d*-glucosido-*dl*-*o*-chloromandelic acid and (2) the tetra-acetyl-*d*-glucose ester and β-tetra-acetyl-*d*-glucosido-*dl*-*p*-methylmandelic acid.

The influence of sodium, potassium, and calcium chlorides, boric, oxalic, acetic, and tartaric acids, borax, potassium oxalate and nitrate, sodium hydroxide, and ammonium molybdate on the rotatory powers of menthol-α-glucoside and of the two β-glucosides, salicin and amygdalin, has been investigated. With the two β-glucosides, the rotation is affected appreciably only by borax and sodium hydroxide, whilst borax has no effect in the case of menthol-α-glucoside. Thus, combination and adsorption appear to take place to a far less extent between glucosides and salts or similar compounds than is the case with the free sugars.

That the sugar of amygdalin is not cellobiose (A., 1920, i, 857) has been confirmed by Zemplén (A., 1920, i, 559). Attempts have now been made to prepare hepta-acetylmaltosido-*dl*-mandelic acid, $CO_2H{\cdot}CHPh{\cdot}O{\cdot}C_{12}H_{14}O_{10}Ac_7$, from the silver salt of inactive mandelic acid and acetobromomaltose, and an amorphous product showing approximately the proper composition and the expected

reactions has been obtained, but the yield was so small that purification could not be effected; the melting point and optical rotation are, however, markedly similar to those of acetylamygdalinic acid and quite different from those of acetylcellosidomandelic acid.

Ethyl β-*tetra-acetyl*-d-*glucosidothiolacetate*,

$$CO_2Et\cdot CH_2\cdot S\cdot C_6H_7O_5Ac_4,$$

forms long, white needles, m. p. 63°, $[\alpha]_D^{15} - 58{\cdot}52°$ (in chloroform).

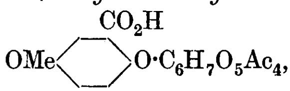
β-d-*Glucosidothiolacetic acid*, $CO_2H\cdot CH_2\cdot S\cdot C_6H_{11}O_5$, forms crystals, m. p. 148—150°, $[\alpha]_D - 66{\cdot}19°$ (in water).

Tetra-acetylglucose ester of p-*hydroxybenzoic acid*,

$$OH\cdot C_6H_4\cdot CO_2\cdot C_6H_7O_5Ac_4,$$

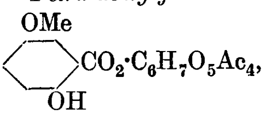
forms white crystals, m. p. 197°, $[\alpha]_D^{20} - 29{\cdot}76°$ (in chloroform), and the isomeric *ester* of *m*-hydroxybenzoic acid, small, white needles, m. p. 147°, $[\alpha]_D^{20} - 26{\cdot}61°$ (in chloroform).

2-β-*Tetra-acetyl*-d-*glucosidoxy*-5-*methoxybenzoic acid*,



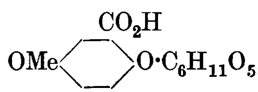
forms slender, white needles, m. p. 172—174°, $[\alpha]_D^{20} - 31{\cdot}76°$ or $- 32{\cdot}13°$ (in chloroform).

Tetra-acetylglucose ester of 5-*methoxy*-2-*hydroxybenzoic acid*,



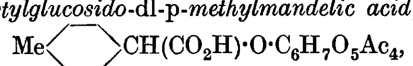
crystallises in needles, m. p. 163°, $[\alpha]_D^{20} - 40{\cdot}20°$ (in chloroform).

2-β-d-*Glucosidoxy*-5-*methoxybenzoic acid*,



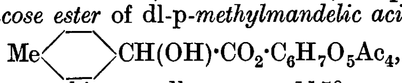
prepared by hydrolysing its tetra-acetyl derivative by means of barium hydroxide solution, forms slender, white needles, m. p. 166°, $[\alpha]_D^{20} - 39{\cdot}63°$ or $- 39{\cdot}18°$ (in water), and gives no coloration with ferric chloride. Its *methyl* ester forms crystals, m. p. 83°, $[\alpha]_D^{20} - 48{\cdot}52°$ or $- 48{\cdot}24°$ (in water).

β-d-*Tetra-acetylglucosido*-dl-p-*methylmandelic acid*,



forms a felted mass of small, white needles, m. p. 149—150°.

Tetra-acetylglucose ester of dl-p-*methylmandelic acid*,



crystallises in snow-white needles, m. p. 115°.

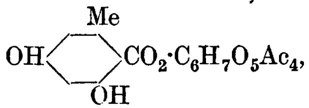
o-*Chlorobenzaldehydecyanohydrin*, $C_6H_4Cl\cdot CH(OH)\cdot CN$, is obtained as an unstable oil, and on hydrolysis yields o-*chloromandelic acid*, $C_6H_4Cl\cdot CH(OH)\cdot CO_2H$, which forms crystals, m. p. 84—85°.

β-d-*Tetra-acetylglucosido*-o-*chloromandelic acid*,

$$C_6H_4Cl\cdot CH(CO_2H)\cdot O\cdot C_6H_7O_5Ac_4,$$

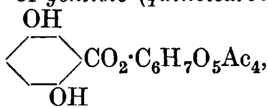
crystallises in white needles, m. p. 182°.

Tetra-acetylglucose ester of *orsellinic acid*,



crystallises in felted, white needles, m. p. 153°, $[\alpha]_D^{18}$ − 41·75° or − 41·40° (in chloroform).

Tetra-acetylglucose ester of *gentisic* (*quinolcarboxylic*) *acid*,



forms white needles, m. p. 185°, $[\alpha]_D^{18}$ − 39·82° or − 39·7° (in chloroform).

Hepta-acetylmaltosido-dl-*mandelic acid*,

$$CO_2H{\cdot}CHPh{\cdot}O{\cdot}C_{12}H_{14}O_{10}Ac_7$$

(impure), has m. p. 68—85°, $[\alpha]_D$ + 9° to + 35° (in chloroform).

T. H. P.

Production of Aldehyde by Chlorophyll and by Aniline Dyes in the Presence of Sunlight. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, **5**, 511—513).—A freshly-prepared solution of chlorophyll in carbon tetrachloride was sprayed on to filter paper and allowed to dry. By repeated spraying and drying, the paper acquired a green colour comparable to that of a leaf.

Bell jars were lined with the moistened chlorophyll paper thus prepared, placed over glass plates and sealed by means of vaselin. On each glass plate, a Petri dish containing 5 c.c. of water was placed. After exposure to sunlight, the water in the Petri dish was tested for aldehyde with positive results. Controls kept in the dark gave negative results in every case. A number of aniline dyes, notably methyl-green and aniline-green, gave similar results. The presence or absence of carbon dioxide was without influence on the result. Oxygen was, however, necessary, and it is concluded that the production of aldehyde is due to the decomposition of chlorophyll (cf. A., 1906, ii, 299).

G. W. R.

Gallotannin. XII. MAXIMILIAN NIERENSTEIN, CHARLES WILLIAM SPIERS, and ARTHUR GEAKE (T., 1921, **119**, 275—286).

2 : 2-Dimethylchroman. L. CLAISEN (*Ber.*, 1921, **54**, [*B*], 200—203).—It has been found that monohydric phenols condense with butadienes under suitable conditions with the formation of products which are insoluble in alkali in addition to phenolic compounds; thus phenol and β-methylbutadiene (isoprene) gave a substance, b. p. 225°, which from its properties and mode of formation appeared to be 2 : 2-dimethylchroman, $C_6H_4{<}\begin{matrix}CH_2{\cdot}CH_2\\ O{-}{-}CMe_2\end{matrix}$. This supposition has been confirmed by the synthesis of the latter, which is found to be identical with the condensation product.

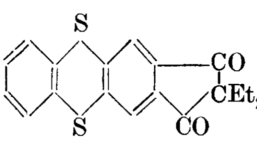
[With O. TIETZE.]—Coumarin is converted by protracted treatment with alcoholic sodium ethoxide solution into ethyl *o*-hydroxycinnamate, m. p. 87°, which is smoothly reduced by hydrogen in alcoholic solution, and in the presence of palladous chloride to ethyl *o*-hydroxyphenylpropionate, m. p. 36—36·5°. The latter is transformed by an excess of magnesium methyl iodide into *β-hydroxy-δ-o-hydroxyphenyl β-methyl-butane*, $HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, prisms, m. p. 112—112·5°, which is readily converted by short warming with dilute sulphuric acid into 2 : *2-dimethylchroman*, colourless, highly refractive liquid, b. p. 98—98·5°/11·5 mm., 225·2—225·4°/769 mm., D_{15}^{15} 1·009. H. W.

Phenolcitraconein. SRI KRISHNA and FRANK GEO. POPE (T., 1921, **119**, 289—291).

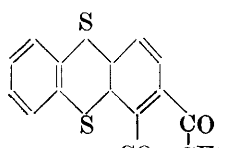
Synthesis and Constitution of Meconic Acid. H. THOMS and R. PIETRULLA (*Ber. deut. Pharm. Ges.*, 1921, **31**, 4—19).—Proof of the constitution of meconic acid as 3-hydroxy-γ-pyrone-2 : 6-dicarboxylic acid, and of its close relationship to chelidonic acid was furnished by a synthesis from acetonyldioxalic ester. This substance on bromination in chloroform solution gave a monobromo-substitution product which immediately lost water and was converted into *monobromochelidonic ester* (*ethyl 3-bromo-γ-pyrone-2 : 6-dicarboxylate*) forming colourless crystals, m. p. 68°. The replacement of bromine by hydroxyl in this compound without far-reaching decomposition presented great difficulty, but a 35% yield of potassium meconate was obtained by the action of a slight excess of 5% potassium hydroxide on an acetone solution of the bromo-ester. The identity of the synthetic acid with meconic acid was confirmed by the preparation of the silver salt and the diethyl ester. G. F. M.

Synthesis of Indanediones. VIII. Indanedione Derivatives of Thianthren. KARL FLEISCHER and JOHANN STEMMER (*Annalen*, 1921, **422**, 265—272).—The replacement of aromatic hydrocarbons by heterocyclic compounds in the synthesis of indanediones has previously proved unsuccessful. The action of pyridine or quinoline on diethylmalonyl chloride results in loss by the latter of hydrogen chloride (A., 1910, i, 490), whilst thiophen and substituted malonyl chlorides, although they interact according to the Friedel and Crafts' reaction, yield only acyclic mono- and di-ketones (A., 1910, i, 490; 1914, i, 48). The authors find, however, that thianthren is capable of yielding indanedione derivatives.

The action of thianthren (1 mol.) on diethylmalonyl chloride (1 mol.) may lead to the formation of two compounds of the constitutions I and II. Actually the reaction gives only one *compound*, $C_{19}H_{16}O_2S_2$, which crystallises in lemon-yellow, oblique prisms, m. p. 135—136°, and gives



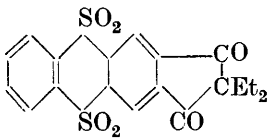
(I.)



(II.)

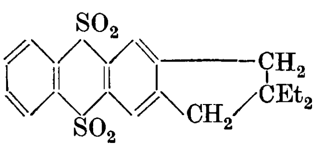
with concentrated sulphuric acid a dirty, bluish-black coloration turning to red on addition of a trace of dilute nitric acid. This compound is probably the thianthrendiethylindanedione of formula I. Treatment of the compound with hydrogen peroxide in acetic acid solution yields

Thianthrendisulphonediethylindanedione (annexed formula), $C_{19}H_{16}O_6S_2$, which crystallises in long, pale yellow needles, m. p. 213—215°, but is not converted into the corresponding selenanthrendiethylindanedione when fused with selenium (compare Krafft and Kaschau, A., 1896, i, 297).



Reduction of thianthrendiethylindanedione by means of amalgamated zinc and hydrochloric acid (D 1·14), (compare Clemmensen, A., 1913, i, 733) yields the corresponding *thianthrendiethylhydrindene*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{S}{S}}{>}C_6H_2{<}{\genfrac{}{}{0pt}{}{CH_2}{CH_2}}{>}CEt_2$, which is a viscous, yellow oil b. p. 277—278°/16 mm. If the reduction is effected by means of phosphorus and hydriodic acid, the resulting product is a *compound*, $C_{19}H_{16}O_2S_2$, m. p. 104—106°, with previous sintering, only one of the two ketonic groups of the indandione being attacked.

Condensation of thianthrendiethylhydrindene with diethylmalonyl chloride yielded only an oil decomposing when distilled in a vacuum. Oxidation of the hydrindene by means of hydrogen peroxide in acetic acid solution gives *thianthrendisulphonediethylhydrindene*, $C_{19}H_{20}O_4S_2$ (annexed formula), which crystallises in small, white needles, m. p. 191—192°.



Conditions have been established by the authors for the preparations of thianthren which give a better yield than the method of Genvresse (A., 1897, i, 240) and are simpler than that given by Fries and Vogt (A., 1911, i, 555).

Dimethylthianthren (compare Genvresse, *loc. cit.*) forms a red oil, b. p. 244°/17 mm., and, when condensed with diethylmalonyl chloride, gives an oil decomposing on distillation in a vacuum.

T. H. P.

Action of Bromine on Dihydroquinine and Dihydrocupreine. RICHARD WELLER (*Ber.*, 1921, **54**, [*B*], 230—238).—Dihydroquinine hydrobromide is converted by bromine in the presence of absolute alcohol into *dihydroquinine dibromide hydrobromide*, $C_{20}H_{26}O_2N_2Br_2,HBr$; the corresponding *sulphate* and *hydrochloride* and the *hydrochloride* and *hydrobromide* of *dihydrocupreine dibromide* are also described. They are yellow or orange-yellow, anhydrous, crystalline substances the melting points of which cannot be determined by reason of decomposition. When they are treated with warm water, one ionisable bromine atom is

eliminated as hydrogen bromide, whilst the second bromine atom replaces a hydrogen atom in position 5 of the benzene nucleus (the substances are oxidised by nitric acid to cinchomeronic acid). The following salts are thus obtained: *bromodihydrocupreine dihydrobromide*, $C_{19}H_{23}O_2N_2Br,2HBr,2{\cdot}5H_2O$, m. p. 248—253°; *bromodihydrocupreine hydrobromide sulphate*,

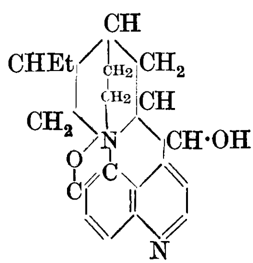
$$(C_{19}H_{23}O_2N_2Br,HBr)_2,H_2SO_4,H_2O,$$

m. p. 224—226°; *bromodihydrocupreine hydrobromide hydrochloride*, $C_{19}H_{23}O_2N_2Br,HBr,HCl,4H_2O$, m. p. 245—248°. It is remarkable that the action of water on the dibromides of dihydroquinine and dihydrocupreine followed by neutralisation of the product yields the same *bromodihydrocupreine hydrobromide*,

$$C_{19}H_{23}O_2N_2Br,HBr,3{\cdot}5H_2O,$$

m. p. 91—92°, so that the methyl radicle of the methoxy-group must have been eliminated by treatment with water; a similar instance has been observed by Christensen (A., 1917, i, 51) in an investigation of the action of chlorine and water on quinine, and has been explained as due to the influence of hypochlorous acid; it has been found that a precisely similar action occurs between chlorine and *p*-methoxyquinoline. The latter substance, however, is not transformed into *p*-hydroxyquinoline under the action of bromine. The salts of monobromodihydrocupreine are well-crystallised substances, the acid compounds being coloured, whilst the normal derivatives are colourless or orange-yellow when anhydrous. The melting points are not definite. They couple with diazonium compounds, although the *ortho*-position to the hydroxyl group is occupied. Sodium acetate solution merely precipitates the normal salts from solutions of bromodihydrocupreine salts, but the free *base*, $C_{19}H_{23}O_2N_2Br,H_2O$, can be prepared by the use of alcoholic potassium hydroxide solution. The bromine atom becomes ionisable when the base is boiled with water or heated at 120—130° and the bromide of an ammonium base, $C_{19}H_{23}O_2N_2Br,2H_2O$, m. p. 89—92°, is produced, for which the name *dihydrocupreonium bromide* is proposed.

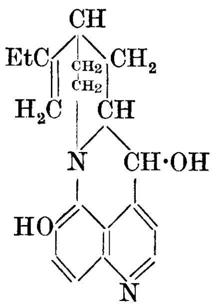
When solutions of bromodihydrocupreine salts are warmed with sodium hydroxide and ammonium chloride, *dihydrocupreonium oxide* (annexed formula), m. p. 228—230°, is formed. The constitution of the substance is deduced from the observations that it is insoluble in alkali, does not contain the keto-group, is not reduced by hydrogen and palladium, is stable towards permanganate in neutral solution, is oxidised to cinchomeronic acid by nitric acid, is not affected by boiling aqueous potassium hydroxide solution, and does not couple with diazonium solutions. Its solutions in acids decolorise permanganate, so that the oxygen bridge



appears to be broken by the acid and a hydroxyl group is formed at the atom 6 (this is further supported by the observed solubility of the

salts in alkali). The preparation of the salts is somewhat difficult, since they could not be obtained with dibasic acids, and those derived from monobasic acids are frequently difficult to crystallise. The *salicylate*, $C_{19}H_{22}O_2N_2,C_7H_6O_3$, m. p. 173—175°, and the *chloride*, $C_{19}H_{23}O_2N_2Cl$, m. p. 255—258°, are described.

When dihydrocupreonium oxide is boiled with alcoholic potassium hydroxide solution in the presence of ammonium chloride, a *substance* (annexed formula), m. p. 240—242°, is obtained in place of the toxin expected. It is soluble in alkali and decolorises potassium permanganate solution. The salts with mono- and di-basic acids are crystalline. Acetylation and benzoylation indicate the presence of two different hydroxyl groups. An attempt to prove the presence of the new double bond by reduction with hydrogen and palladous chloride was unsuccessful. The following derivatives have been prepared: *chloride*, $C_{19}H_{22}O_2N_2,2HCl,3H_2O$, m. p. 98—102°; *sulphate*, $(C_{19}H_{22}O_2N_2)_2,H_2SO_4$; *oxalate*, $C_{19}H_{22}O_2N_2,H_2C_2O_4$, m. p. 203—204°; *picrate* of *acetyl* compound, $C_{19}H_{21}O_2N_2Ac,C_6H_3O_7N$, m. p. 159—161°; *benzoyl* compound, $C_{19}H_{21}O_2N_2Bz$, m. p. 121—125°.



H. W.

Preparation of Hydrogenated Cinchona Alkaloids containing Selenium. VEREINIGTE CHININFABRIKEN ZIMMER & CIE (D.R.P., 331145; from *Chem. Zentr.*, 1921, ii, 449).—Selenium dioxide is brought into reaction with hydrogenated cinchona alkaloids or their derivatives in the presence of concentrated sulphuric acid and the products of the reaction are diluted with water and boiled. *Selenohydroquinine*, from hydroquinine sulphate or hydroquinine sulphuric ester, forms yellow needles which remain unchanged below 235°; *selenoethylhydrocupreine*, yellow needles, m. p. 233—234°, and *selenohydrocupreine*, small, orange-coloured needles which do not melt below 235°, are also described. The products are useful therapeutically. H. W.

Process for obtaining the Active Ingredient of *Lobelia inflata*. C. H. BOEHRINGER & SÖHNE (Brit. Pat. 145621).—The plant when extracted with alcohol, ether, or benzene, and the extractive matter purified by transference to dilute acid solution and back to ether, furnishes a crude lobeline, which actually contains at least three alkaloids—*α-lobeline*, $C_{21}H_{23}O_2N$, colourless crystals, m. p. 120°, having the characteristic physiological action of *Lobelia inflata*; *β-lobeline*, non-crystalline, and characterised by a hydrochloride, soluble with difficulty in water; and *γ-lobeline*, non-crystalline. α- and β-Lobeline give also sparingly soluble mercurous double salts, which if desired may serve for the purification of the bases. For the isolation of pure α-lobeline the crude

alkaloids, obtained as above, are dissolved in dilute hydrochloric acid, and after keeping β-lobeline hydrochloride crystallises out, and α-lobeline hydrochloride is extracted from the solution by repeated agitation with chloroform, the chloroform solution is shaken with sodium hydroxide, and the chloroform evaporated to dryness with caution. The residue crystallises on keeping a short time, and the base may if necessary be recrystallised from ether.

G. F. M.

Action of γ-Bromovaleric Acid on Amines. BRUNO EMMERT and ERNST MEYER (*Ber.*, 1921, **54**, [*B*], 210—213).—1-Phenyl-5-methylpyrrolidone (compare Emmert, A., 1907, i, 399) has been synthesised by the action of aniline on γ-bromovaleric acid, but a similar method does not appear to be applicable to aliphatic amines or amides, which, under these conditions, give valerolactone. The latter substance seems to be the preliminary product of the action of amines on the bromo-acid, and, if this is the case, it should be possible to synthesise 1-aryl-5-methylpyrrolidones from valerolactone and the arylamine. Reaction, however, does not occur when the components are heated together for some hours at 220°, but proceeds readily and smoothly when a little hydrogen bromide or chloride is added to the mixture, the change probably depending on the gradual conversion of the lactone into the halogeno-acid.

1-Phenyl-5-methylpyrrolidone, m. p. 319·5° (corr.), is obtained in 67% yield by heating a mixture of valerolactone, aniline, and aniline hydrochloride at 210° during twenty minutes. 1-o-*Tolyl-5-methylpyrrolidone* is a colourless oil, b. p. 318° (corr.), whilst the corresponding p-*isomeride* crystallises in needles, m. p. 82—83°, b. p. 192°/14 mm. 1-m-*Nitrophenyl-5-methylpyrrolidone* forms pale yellow needles grouped in clusters, m. p. 54—56°. H. W.

Compounds of Pyridine with the Alkali Metals. IV. BRUNO EMMERT and RUDOLF BUCHERT (*Ber.*, 1921, **54**, [*B*], 204—209).—The constitution of pyridine sodium (Emmert, A., 1916, i, 668; 1917, i, 221) is expressed by the formula,

$$Na \ . \ . \ . \ NH_5C_5 \ . \ . \ . \ C_5H_5N \ . \ . \ . \ Na,$$

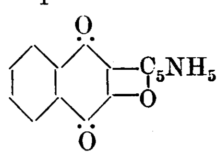
with the proviso that the substance can react in a number of tautomeric forms. If this is the case, it should be convertible by alkyl haloids into dialkyltetrahydrodipyridyls (Hofmann, A., 1881, 921; Emmert, A., 1909, i, 602; 1917, i, 221; 1919, i, 455; 1920, i, 331). This has been tested in the cases of methyl iodide, ethyl bromide, and benzyl chloride. On account of the extraordinary reactivity of the dialkyl compounds, their isolation as such was not found to be possible, but their formation is clearly demonstrated by their characteristic behaviour depending on their dissociation into radicles with quadrivalent nitrogen (A., 1920, i, 331). In addition, the formation of *N*-benzylpyridinium iodide (isolated as the platinichloride) has been shown to occur when iodine is added to the product of the action of benzyl chloride on sodium pyridine.

Dipyridine sodium, $Na,2C_5H_5N$, readily loses a molecule of pyridine when warmed in a vacuum and yields monopyridine sodium, which, however, readily re-absorbs pyridine with formation of the di-derivative. The mono-compound can also react with aniline or dimethylaniline, yielding the greenish-black *anilinomonopyridine sodium* and *dimethylanilinomonopyridine sodium* respectively. Since the dipyridine derivative readily parts with two molecules of the base without fundamental change in the properties of the original substance, it appears probable that two molecules of pyridine are attached directly to the sodium atom and the two farther molecules are united to the pyridine sodium complex thus, $Na \ldots NH_5C_5 \ldots C_5H_5N \ldots Na,2C_5H_5N$, the anilino- and dimethylanilino-compounds being similarly constituted. Evidence is also adduced which points to the ability of pyridine sodium to unite with more than two molecules of pyridine.

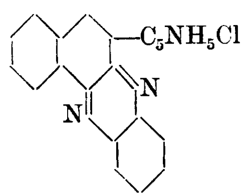
1·52 Grams of dipyridine sodium are contained in 100 c.c. of the pyridine solution saturated at the laboratory temperature.

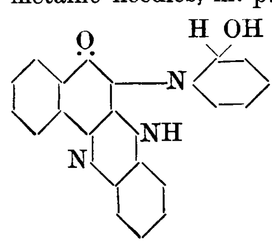
H. W.

Investigation of 2 : 3-Dichloro-α-naphthaquinone. FRITZ ULLMANN and MARGARETE ETTISCH (*Ber.*, 1921, **54**, [*B*], 259—272).—2 : 3-Dichloro-α-naphthaquinone (compare Weichhardt, *Inaug. Diss.*, Freiburg, 1888), the preparation of which, by the sulphonation of α-naphthol and subsequent treatment of the product with potassium chlorate and concentrated hydrochloric acid, is fully described, crystallises in long, yellow needles, m. p. 193°, and is readily converted by warm pyridine into the *anhydride* of 3-*hydroxy-α-naphthaquinone*-2-*pyridinium* (annexed formula), pale yellow needles, m. p. 292°.



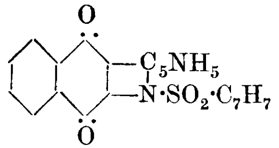
The latter substance is oxidised by permanganate to pyridine and phthalic acid and readily yields a *phenylhydrazone*, $C_{21}H_{15}O_2N_3$, yellowish-red needles, m. p. 253°, and an *oxime*, $C_{15}H_{10}O_3N_2$, yellow, matted needles, m. p. about 244°, after some previous decomposition. When warmed with *o*-phenylenediamine in hydrochloric acid solution, it gives 1-*hydroxynaphthazine*-2-*pyridinium chloride*, red, shining metallic needles, m. p. about 305°, which yields a readily hydrolysed *dichloride* and is transformed by sodium hydroxide solution through the corresponding ammonium base to the oxy-dihydro-*compound* (annexed formula) small, yellow, feathery crystals, m. p. about 310°.





Further proof of the constitution of the yellow anhydride is afforded by the observation that the *anhydride* of 3-p-*toluenesulphamino-α-naphthaquinone*-2-*pyridinium*

(annexed formula), bright red shining needles, m. p. 250°, is



obtained by the action of toluene-sulphonamide and pyridine on 2 : 3-dichloro-α-naphthaquinone; this substance is hydrolysed by boiling dilute sodium hydroxide solution or by concentrated hydrochloric acid to the anyhdride, m. p. 292°, and *p*-toluenesulphonamide or *p*-toluenesulphonyl chloride respectively.

2 : 3-Dichloro-α-naphthaquinone reacts with potassium phenoxide at 100° to yield 2 : 3-*diphenoxy-α-naphthaquinone*, orange-yellow needles, m. p. 205°, the vat from which has no affinity for cotton; with catechol in the presence of diethylaniline it gives *α-naphthaquinonebenzodioxine*, $C_{10}H_4O_2{<}{}^{O}_{O}{>}C_6H_4$, long, reddish-violet needles, m. p. 280°, whilst with alizarin in the presence of pyridine it yields *α-naphthaquinone*-1 : 2-*anthraquinonedioxine*,

$$C_{10}H_4O_2{<}{}^{O}_{O}{>}C_{14}H_6O_2,$$

red crystals, m. p. about 375°, which gives reddish-brown shades on cotton from a brownish-red vat. *p*-Toluenesulphonyl-*o*-aminophenol and pyridine transform 2 : 3 - dichloro - *a* - naphthaquinone into N-p-*toluenesulphonyl-α-naphthaquinonephenoxazine*,

$$C_{10}H_4O_2{<}{}^{N(SO_2\cdot C_7H_7)}_{O}{>}C_6H_4,$$

orange-coloured crystals, decomp. about 130°, which is hydrolysed by cold sulphuric acid to *α-naphthaquinonephenoxazine*, dark blue, shining crystals. 3-*Chloro*-2-*amino-α-naphthaquinone*, yellowish-brown needles, m. p. 193°, is prepared by passing a current of dry ammonia through a solution of 2 : 3-dichloro-α-naphthaquinone in boiling nitrobenzene.

1 : 4-Diacetoxynaphthathioxanthone, long, red needles, m. p. 208° (compare Ghosh and Smiles, T., 1914, **105**, 1396) is prepared by the action of acetic anhydride and zinc chloride on *o*-dihydroxynaphthylthiolbenzoic acid, and is hydrolysed by alcoholic sodium hydroxide solution to 1 : 4-*dihydronaphthathioxanthone*, which is rapidly oxidised by air to *α-naphthaquinonethioxanthone*,

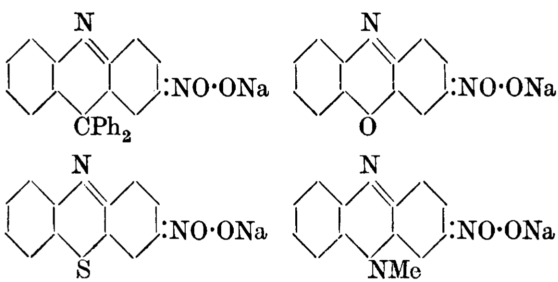
$$C_{10}H_4O_2{<}{}^{S}_{CO}{>}C_6H_4,$$

dark brown needles, m. p. about 310°. H. W.

The Preparation of 9(10)-Phenanthridone from Phenanthrene. LEONE OYSTER and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1921, **43**, 208—210).—Phenanthrene was oxidised to phenanthraquinone, which was in turn converted into diphenic acid, the anhydride of which when boiled with ammonium hydroxide gave diphenamic acid. When this acid was submitted to Hofmann's reaction with sodium hypobromite, the product was not the expected 1′-aminodiphenyl-1-carboxylic acid, but 9(10)-*phenanthridone*, $\begin{matrix} C_6H_4\cdot CO \\ | \quad\quad | \\ C_6H_4\cdot NH \end{matrix}$, m. p. 291°, which, when condensed with

α-chloroanthraquinone, yielded a white, crystalline *compound*, m. p. 82°, and a brick-red, amorphous *compound*. W. G.

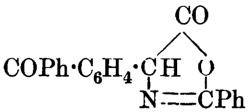
Absorption Spectra of certain Nitro-derivatives of Carbazine, Phenoxazine, and Thiodiphenylamine. F. Kehrmann and Henri Goldstein (*Helv. Chim. Acta*, 1921, **4**, 26—31).—The authors have investigated the absorption spectra of a number of nitro-compounds in alcoholic sodium hydroxide solution, in which they exhibit an intense characteristic coloration clearly differentiated from that of the solid compounds. This property is shown only by compounds possessing at least one nitro-group in the para position to the cyclic nitrogen atom (compare Kehrmann and Nossenko, A., 1913, i, 1230). The compounds examined comprise: 3-nitrodiphenylcarbazine, 3-nitrophenoxazine, 3-nitrothiodiphenylamine, 1(?):3-dinitrodiphenylcarbazine, 1:3-dinitrophenoxazine, 1 : 3-dinitrothiodiphenylamine, 3 : 6-dinitrodiphenylcarbazine, 3 : 6-dinitrophenoxazine, 3 : 6-dinitrothiodiphenylamine, 1 : 3 : 6-trinitrodiphenylcarbazine, 1 : 3 : 6-trinitrophenoxazine, 1 : 3 : 6-trinitrothiodiphenylamine, 1 : 3 : 6 : 8-tetranitrodiphenylcarbazine, 1 : 3 : 6 : 8-tetranitrophenoxazine, 1 : 3 : 6 : 7-tetranitrophenoxazine, 1 : 3 : 7-trinitrophenoxazine, 1 : 3 : 5 : 7-tetranitrophenoxazine, 1 : 3 : 6 : 8-tetranitrodiphenylcarbazine dinitrated in the phenyl groups, and 1 : 3-dinitromethyldihydrophenazine. All these substances are derived from one or other of the four chromogens:



The absorption curves show that the tints of the alkaline solutions deepen in the order of the groups, CPh_2, O, S; of derivatives substituted in the same positions, the thiodiphenylamine derivatives are the most, and those of carbazine the least, intensely coloured. In the only case studied, replacement of the sulphur atom by a methylimino-group was found to cause further deepening of the colour. With similar positions of the nitro-groups, the absorption spectra for the three series are analogous in form. The introduction into the chromogenic group of a nitro-group in the para position to the cyclic nitrogen atom deepens the tint, whereas if the nitro-group enters another position the effect is often strongly hypsochromic (compare Misslin and Bau, A., 1919, i, 555). Introduction of fresh nitro-groups into para-nitro-derivatives always lightens the tint to an extent depending on the position assumed. The red coloration of alcoholic alkaline solutions of asymmetric mono- and di-

nitrodiphenylcarbazines appears clearly only in the hot, the transformation into nitronic salt being scarcely perceptible at the ordinary temperature. T.H.P.

A Lactimonic Derivative of Aminophenylacetic Acid. ST. MINOVICI and V. THÜRINGER (*Bul. Soc. Chim. România*, 1920, **2**, 13—20).—During the benzoylation of aminophenylacetic acid (this vol. i, 244) a second *compound*, $C_{22}H_{15}O_3N$, m. p. 123°, is obtained, which is not decomposed by boiling with 10% hydrochloric acid, but is decomposed by 20% potassium hydroxide, giving a mixture of mandelic and benzoic acids. With phenylhydrazine in ether it gives a *phenylhydrazone*, m. p. 191°. When warmed in alcoholic solution with hydrazine hydrate it gives a *compound*, m. p. 176°. In view of its behaviour, therefore, the authors consider the compound, m. p. 123°, to be *5-keto-2-phenyl-4-benzoylphenyldihydro-oxazole* (annexed formula).



W. G.

***o*-Quinones and 1 : 2-Diketones. II. Action of Aqueous Ammonia on Benzils in the Absence of Air.** A. SCHÖNBERG (*Ber.*, 1921, **54**, [*B*], 242—244. Compare preceding abstract.)—The action of ammonia on benzil has been investigated frequently and imabenzil, $C_{35}H_{28}O_3N_2$, benzilimide, $C_{21}H_{17}O_2N$, and triphenyloxazole (benzilam), $C_{21}H_{15}ON$, have been identified among a large number of difficultly separable compounds. The latter substance, m. p. 114—115°, and ammonium benzoate are now shown to be produced in almost quantitative amount when benzil is heated in a sealed tube with concentrated aqueous ammonia at 120°. The course of the reaction is represented by the equations,

$$COPh{\cdot}COPh + H_2O \rightarrow Ph{\cdot}CHO + Ph{\cdot}CO_2H$$

and $$COPh{\cdot}COPh + Ph{\cdot}CHO + NH_3 \rightarrow CPh{<}\begin{matrix}O-CPh\\ \| \\ N-CPh\end{matrix} + 2H_2O,$$

and the innovation of the present series of experiments consists in working under such conditions that the reaction mixture is shielded from contact with air, and oxidation of benzaldehyde is avoided.

[With D. ROSENTHAL].—*p*-Anisil is transformed by aqueous ammonia at 120° into *tri*-p-*anisyloxazole*, colourless rods, m. p. 140°, whilst *p*-tolil yields *tri*-p-*tolyloxazole*, colourless prisms, m. p. 145°, and ammonium *p*-methylbenzoate. H. W.

Influence of Negative Groups of Different Character on the Reactivity of Hydrogen Atoms Carried by the Same Carbon Atom. I. BIRAJ MOHAN GUPTA (T., 1921, **119**, 298—304).

The Iodoamidines. J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1921, **172**, 452—454. Compare A., 1920, i, 568).—Further evidence is given in support of the view that iodobenzamidine is

a derivative of hypoiodous acid. It reacts quantitatively with antipyrine to give iodoantipyrine, with vanillin to give iodovanillin, and with thymol to give iodothymol. When added gradually to acetic anhydride it gives a *compound*, $C_7H_6N_2I_2,OAc_2$, m. p. 135°, which is apparently a derivative of di-iodobenzamidine and acetic anhydride. The whole of its iodine is liberated by potassium iodide and hydrochloric acid. It is decomposed by water, giving free iodine. W. G.

Additive Compounds of Antipyrylaminodiacetic Acid and its Salts with Neutral Salts. ROBERT GEORGE FARGHER and HAROLD KING (T., 1921, **119**, 292—298).

Isatin-5-sulphonic Acid. J. MARTINET and O. DORNIER (*Compt. rend.*, 1921, **172**, 330—331).—When isatin is dissolved in fuming sulphuric acid containing 20% of sulphuric anhydride and the mixture warmed on a water-bath for half an hour, isatin-5-sulphonic acid is formed which is identical with that obtained by the oxidation of the sodium salt of indigotin-5 : 5′-disulphonic acid. Isatin-5-sulphonic acid gives a *phenylhydrazone*, m. p. 270° (decomp.), which yields a yellow *barium* and a citron-yellow *potassium* salt. With hydroxylamine potassium isatinsulphonate gives an *oxime*. [See, further, *J. Soc. Chem. Ind.*, 1921, April.] W. G.

The Colour of the Indigoids. J. MARTINET (*Rev. Gén. Mat. Col.*, 1921, **25**, 17—18).—In spite of the accumulated evidence with regard to the relation between colour and chemical constitution of compounds, it is still impossible to express this relationship in a general manner by a mathematical formula, and to calculate selective absorption. Certain rules, however, permit the colour of organic compounds to be predicted with reasonable probability, as may be demonstrated in the case of the indigoids. Thus, there is an increase in the depth of colour in passing from brownish-red *iso*indigotin (3:3′-bisindole) to violet-red indirubin and blue indigotin; a similar relationship exists in the case of oxindigo (2 : 2′-biscoumarone), thioindigo (2 : 2′-bisoxythionaphthen) and indigotin; substituents in the 6 : 6′-positions, such as methyl, hydroxyl, amino-, and the halogens, lessen the depth of colour.

Facts such as these are not isolated cases, and could be predicted by the application of the following rules:

(*a*) The union of an auxochrome and a chromophore by means of a chain of conjugated double bonds between carbon leads to an increase in the depth of colour (bathochromic effect).

(*b*) The direct union of a chromophore and an auxochrome decreases the depth of colour (hypsochromic effect).

This first rule arises from the examination of a large number of compounds of established constitution, but the second is less well known. For example, the group NO is a powerful chromophore, and NHEt is a powerful auxochrome. When these groups are united by a benzene ring the deeply coloured *p*-nitrosomonoethylaniline results (*a*), whereas when these groups are directly united the almost colourless nitrosoamine of monoethylaniline results (*b*). In the case of *iso*indigotin, the auxochrome NH groups being

directly attached to the chromophore, CO groups are in an unfavourable position for the production of colour, whilst in indigotin the NH group exerts its maximum effect because it is attached to the CO group by a benzene nucleus on one side, and by a carbon atom, which forms part of a chain with double conjugated bonds, on the other. The formula of indirubin occupies an intermediate position between the two, and this fact is reflected in its colour. The increase in the depth of colour in passing from oxindigo to thioindigo and indigotin is a bathochromic effect due to the increasing power of the auxochromes OPh—, SPh—, NHPh—, and is in agreement with known facts in other series.

With regard to the diminution in the depth of colour produced by the introduction of auxochromes in positions 6 : 6′-, it appears that (*c*) the effect of two auxochromes is cumulative when in the para-position, but that they act in contrary directions when in the meta-position with respect to one another. This also is in agreement with experience in other series, thus *o*-nitro-*p*-phenylenediamine is greenish-black, whilst *o*-nitro-*m*-phenylenediamine is yellowish-red, and nitroquinol is red whilst *as*.-nitroresorcinol is lemon-yellow in colour. This rule is particularly well exemplified in the indigoid series, for all 5 : 5′-derivatives are considerably deeper in colour than the corresponding 6 : 6′-derivatives. The application of these three rules serves as an excellent guide in the search for new colouring matters of a desired shade. F. M. R.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. BADISCHE ANILIN & SODA-FABRIK (D.R.P., 329246; from *Chem. Zentr.*, 1921, ii, 314).—2-Arylaminoanthraquinones, their derivatives, homologues, or substitution products, or such 2-substituted derivatives of anthraquinone (for example, anthraquinone-2-sulphonic acids or 2-halogenoanthraquinones) as can pass into 2-arylaminoanthraquinones under the conditions of the reaction, are heated to a high temperature with primary aromatic amino-compounds in the presence of alkaline condensing agents and, preferably, of oxidising substances particularly, oxygen, or air. Azine-like products of the constitution, anthraquinone$<{NAr \atop NH}>$Ar, are produced which are used in the preparation of coloured varnishes (particularly oil and spirit varnishes) and are important intermediate products in the dye industry. The *substance* from 2-phenylaminoanthraquinone, aniline, and calcium hydroxide at 180°, forms shining bronzy needles; it yields a blue solution in organic media and a bottle-green solution in sulphuric acid. Other examples include the use of anthraquinone-2-sulphonic acid, 2-chloroanthraquinone, and of *p*-toluidine. Copper acetate is added in the case of 2-chloroanthraquinone. H. W.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. BADISCHE ANILIN & SODA-FABRIK (D.R.P., 329247; from *Chem. Zentr.*, 1921, ii, 314. Compare preceding abstract).—1-Halogenoanthraquinones or 1-halogenoanthraquinones which contain a reactive substituent in the *ortho*-

position to the halogen atom, or derivatives of these substances are heated with *o*-aminodiarylamines or their nuclear substituted products either alone or in the presence of solvents or suspending media and with or without the addition of substances which combine with acids and catalytically active materials. Phenylanthraquinonylbenzohydroazines, $C_6H_4<{CO \atop CO}>C_6H_2<{NR \atop NH}>C_6H_4$, are produced similar to those described in the preceding abstract. The *product*, $C_{26}H_{16}O_2N_2$, coppery needles, is prepared from 1-chloroanthraquinone, *o*-aminodiphenylamine hydrochloride, potassium acetate, and naphthalene. The same substance is formed from 1 : 2-dichloroanthraquinone, m. p. 202—204° (from 1-aminoanthraquinone-2-sulphonic acid), and from 1-bromo-2-methoxyanthraquinone, pale yellow needles (by bromination of 2-methoxyanthraquinone in nitrobenzene). Two isomeric *monochloro*-derivatives of the azine, $C_{26}H_{16}O_2N_2$, are prepared from 1 : 5- or 1 : 8-dichloroanthraquinone and *o*-aminodiphenylamine. 1 : 4-Dichloroanthraquinone, on the other hand, loses both chlorine atoms under the influence of *o*-aminodiphenylamine and gives a blue condensation product which is almost insoluble in acetone. 4-Chloro-2-aminodiphenylamine (from 1 : 4-dichloro-2-nitrobenzene) can be used in place of *o*-aminodiphenylamine; a chlorinated azine is thereby formed. H. W.

o-Quinones and 1 : 2-Diketones. I. Explanation of the Anhydride of Acenaphthenequinoneimide as Diacenaphthyleneazotide [Acenaphthylene-1 : 2-azine]. A. SCHÖNBERG and F. NEDZATI (*Ber.*, 1921, **54**, [*B*], 238—242).—The product of the action of ammonia on acenaphthenequinone has been obtained by Graebe in a non-crystalline state, who has assigned to it the formula $C_{24}H_{12}ON_2$ and considered it to be the anhydride of acenaphthenequinoneimide, without, however, advancing any definite evidence in support of his views. The substance has now been obtained in the form of red needles, m. p. above 400° (decomp.) purification being effected either by crystallisation from nitrobenzene or by sublimation over iron filings. The purified material is found to be free from oxygen and to show close resemblance to phenanthrazine, but not to phenanthraquinoneimide anhydride.

$$C_{10}H_6<{C{-}N{-}C \atop C{-}N{-}C}>C_{10}H_6$$

It is therefore considered to be acenaphthylene-1 : 2-azine (annexed formula), and this conception is confirmed by its formation by reduction of acenaphthenequinonedioxime by stannous chloride and hydrochloric acid. H. W.

Stereoisomeric Derivatives of Phenacyl Sulphide. EMIL FROMM and ALFRED EHRHARDT (*Ber.*, 1921, **54**, [*B*], 187—193).—The five stereoisomeric phenylhydrazones and oximes of phenacyl sulphide and sulphone have been described and their configurations elucidated (Fromm and Flaschen, A., 1913, i, 186). The corresponding hydrazones and semicarbazones have now been prepared.

Phenacylsulphidemonohydrazone anhydride, ${N{:}CPh{\cdot}CH_2 \atop N{:}CPh{\cdot}CH_2}>S$, colour-

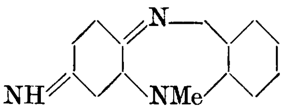
less crystals, m. p. 175°, is obtained by the protracted heating of phenacyl sulphide dissolved in glacial acetic acid with an excess of hydrazine hydrate or by heating either of the hydrazones (see later) with the same solvent. *Phenacyl-sulphide*-syn-*monohydrazone*, m. p. 225°, is prepared by protracted boiling of a solution of the anhydride in dilute alcohol; the anti-*isomeride*, m. p. 128°, is formed from the calculated quantities of the components in alcoholic solution or in the absence of solvent and is converted successively by boiling glacial acetic acid into the *syn* form, m. p. 225°, and the anhydride, m. p. 175°. *Phenacylsulphonemonohydrazone anhydride*, m. p. 206°, is prepared in the same manner as the sulphide derivative and is transformed by dilute alcohol into the syn-*monohydrazone*, m. p. 185°; when treated with benzaldehyde, the latter yields the anhydride, m. p. 206°, instead of the expected benzylidene compound. *Phenacylsulphone*-anti-*monohydrazone* forms colourless crystals, m. p. 158°, and is converted by glacial acetic acid into the *syn* isomeride and the anhydride; its *benzylidene* derivative, yellow crystals, has m. p. 150°.

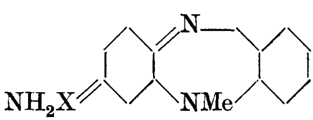
Phenacylsulphonedihydrazone, colourless crystals, m. p. 156° (*dibenzylidene* derivative, yellow crystals, m. p. 178°), *phenacylsulphone*anti*dihydrazone*, m. p. 172° (*dibenzylidene* derivative, yellow crystals, m. p. 194°) and *phenacylsulphone*amphi*dihydrazone*, m. p. 188° (*dibenzylidene* compound, yellow crystals, m. p. 171°) are also described. Protracted treatment with boiling glacial acetic acid solution causes the elimination of a hydrazine residue from each of the dihydrazones with consequent formation of the *syn*-monohydrazone and ultimately of the monohydrazone anhydride. In general, the same rules apply in the preparation of the di- as of the mono-hydrazones; in acetic acid solution, the hydrazine group is introduced in the *syn* position, whilst in faintly alkaline alcoholic solution (containing free hydrazine) it occupies the *anti* position.

Phenacyl-sulphidemonosemicarbazone, m. p. 237°, is obtained by boiling an alcoholic solution of molar quantities of phenacyl sulphide and semicarbazide hydrochloride, whilst, with excess of the latter, the *disemicarbazone*, colourless crystals, m. p. 232°, is produced. *Phenacylsulphonemonosemicarbazone*, m. p. 258°, is prepared in the same manner as the sulphide derivative; an excess of semicarbazide hydrochloride, however, yields NN′-*phenacylsulphone*-1 : 5-*diaminobiuret*, $SO_2<\begin{matrix}CH_2\cdot CPh\colon N\cdot NH\cdot CO\\ CH_2\cdot CPh\colon N\cdot NH\cdot CO\end{matrix}>NH$, m. p. 252°, in place of the expected disemicarbazone. The action of free semicarbazide in boiling alcoholic solution on phenacylsulphone leads to the formation of *phenacylsulphonecarbohydrazone*, $SO_2<\begin{matrix}CH_2\cdot CPh\colon N\cdot NH\\ CH_2\cdot CPh\colon N\cdot NH\end{matrix}>CO$, m. p. 250°. H. W.

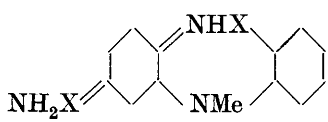
Determination of the Constitution of Coloured Substances from their Absorption Spectra. F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1921, **4**, 31—44. Compare A., 1920, ii, 142).—The absorption spectra of monoamino-derivatives of methyl- and phenyl-phenazine compounds have now been examined.

The first series considered consists of derivatives of the amino-compound of methylphenazine (annexed formula), which is homologous with *apo*-safranine and is soluble in ether and very similar in properties to the paraquinonoid bases of the colouring matters derived from triphenylmethane; the structure given is hence preferable to that previously suggested by Kehrmann on the basis of Nietzki's view of the configuration of the indones ("Organische Farbstoffe," 3rd edition, 213). The formula proposed for colouring matters by Fierz and Koechlin, (A., 1918, i, 549), by Georgievics (A., 1904, i, 351), and by Kaufmann (A., 1904, i, 534) are incapable of explaining the phenomena observed by the authors (compare Hantzsch, A., 1919, ii, 255). The base under consideration is an extremely strong one and is obtained by the action of sodium hydroxide on its mono-acid salt; it passes readily from its ethereal solution to water, even when the latter is saturated with sodium carbonate. It has a bright orange-red colour and is less powerful, colorimetrically, than the mono-acid salt. The latter, being cherry-red, is assumed to retain the paraquinonoid structure of the base, this view being confirmed by the fact that the salt is non-diazotisable (I). The green di-acid salt (II) is derived normally from the mono-acid salt, the fact that the green solution in sulphuric acid is diazotisable being explained on the assumption that this equilibrated solution contains a certain proportion of tri-acid salt. The latter is formed pure only in sulphuric acid containing 40% of anhydride, and is reddish-brown, the form of its absorption spectrum being that of the spectrum of the methylphenazonium di-acid salt; it is hence regarded as of ortho-quinonoid structure (III).

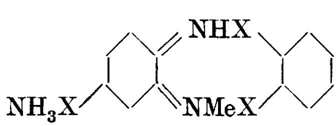




(I.)

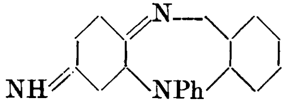


(II.)

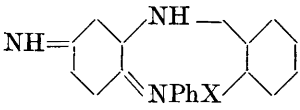


(III.)

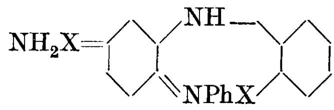
These considerations apply also to *apo*safranine (annexed formula), replacement of the methyl by a phenyl group resulting in a positive displacement of the absorption, that is, displacement of the absorption bands towards the infra-red. The basic properties are weakened, the base showing little tendency to pass from its ethereal solution into aqueous alkali.



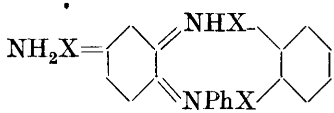
Different conclusions are reached in the case of the isomeride of



(IV.)



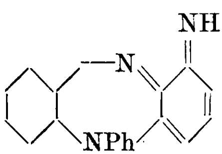
(V.)



(VI.)

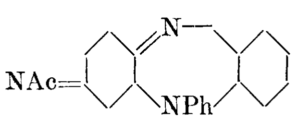
*apo*safranine (IV), the formula of which excludes the possibility of formation of an anhydride base; indeed, when its alkaline solution is shaken with ether, the latter remains colourless. The monoacid- and diacid-salts (V) are accorded para-quinonoid structures because: (1) the conversion of a blue monoacid salt into a green diacid salt is explainable only by the salification of a basic group forming part of the chromogen skeleton; the orthoquinonoid diacid salt would contain a free amino-group, which is improbable, especially in view of the feeble basicity of an azinic nitrogen; (2) the presence of an imino-group is supported by the great stability of the diacid salts. The triacid salt (VI) is reddish-brown.

The second isomeride of *apo*safranine (VII) forms a base which is soluble in ether to a blue solution and has the constitution of an orthoquinoneimine. The monoacid salt is green and is assumed to contain the double linkings of the base, the colour being deepened by fixation of the acid on an imino-group. The diacid salt, like the phenylphenazonium monoacid salt, is lemon-yellow, the imino-group of the monoacid salt being transformed into a salified amino-group; such a group loses almost all auxochromic properties. This view is supported by the fact that the perchlorate is readily diazotised. Finally, the use of 100% acid gives the red tint characterising the phenylphenazonium diacid salt.



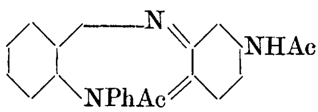
(VII.)

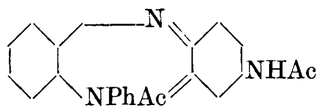
To the base of the acetyl derivative of *apo*safranine (VIII) is ascribed a paraquinonoid configuration, the existence of an internal bridge between a nitrogen atom of the chromogen and an acetylamino-group being regarded as improbable. The base is soluble in ether and the violet monoacid salt yellow. This lightening of the colour is explained by assuming that the monoacid salt has the orthoquinonoid constitution of the phenylphenazonium mono-acid salt, although, on the other hand, the spectra of these two monoacid salts differ somewhat.



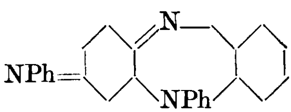
(VIII.)

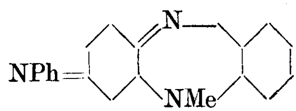
The absorption spectra of the mono- and di-acid salts of acetyl *apo*safranine exhibit striking analogies to those of the corresponding salts of the acetyl derivative of the first isomeride of *apo*safranine. If paraquinonoid structures are attributed to the monoacid-salts in the two cases, the two formulæ are so different that similarity in absorption spectra could not be expected. For this reason these monoacid-salts are regarded as of orthoquinonoid configuration (IX and X), the formulæ then exhibiting the necessary similarity The acetyl derivatives are less intensely coloured than the amino-compounds from which they are derived.


(IX.)


(X.)

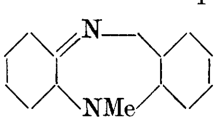
The spectra of the bases XI and XII and of their mono- and

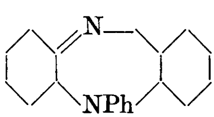

(XI.)


(XII.)

di-acid salts have also been investigated. These render apparent the effect of the anilino-auxochrome in deepening the colour and in favouring the fusion of the extinction bands and the union of the maxima. The presence of the phenyl group appears to render impossible the formation of the orthoquinonoid triacid salt, even when cooled, concentrated acids are employed.

The constant presence in the ultra-violet absorption spectra of these compounds of an absorption band between $\lambda = 270$ and $\lambda = 290$ seems to indicate that this band is produced by the two chromogens (annexed formulæ), independently of the action of the auxochromes.





T. H. P.

Certain Derivatives of Paeonol. ADOLF SONN (*Ber.*, 1921, **54**, [*B*], 358—360).—The recent communications of Adams (A., 1919, i, 160) and of Rennie, Cooke, and Finlayson (T., 1920, 117, 338) have led the author to describe certain derivatives which he had prepared.

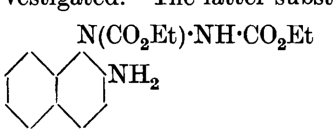
Benzeneazopaeonol, C_6H_5:N:N·C_6H_2Ac(OMe)·OH, shining, brownish-red needles, m. p. 135°, is prepared by the addition of diazotised aniline to a solution of paeonol in an excess of very dilute sodium hydroxide solution. It is reduced by sodium hyposulphite in warm alkaline solution to 3-*aminopaeonol*, yellow needles, m. p. 115°, after slight previous softening (*diacetyl* derivative, short rods, or cubes, m. p. 165°), which is also obtained

from the corresponding nitro-compound (compare Adams, *loc. cit.*). 3-Nitropaeonol condenses with anisaldehyde in the presence of aqueous-alcoholic potassium hydroxide to yield 3-*nitro*-4-*methoxy*-6-*hydroxyphenyl* 4′-*methoxystyryl ketone*,

$$NO_2\cdot C_6H_2(OMe)(OH)\cdot CO\cdot CH\!:\!CH\cdot C_6H_4\cdot OMe,$$

thin, yellow leaflets, m. p. 182°, after slight softening which is reduced by tin and hydrochloric acid in glacial acetic acid solution to the corresponding *amino-ketone* (*acetyl* derivative, needles, m. p. 203°). H. W.

Azodicarboxylic Ester as a Reagent for the Introduction of the Hydrazine Radicle into the Aromatic Nucleus. I. Azo-ester and β-Naphthylamine. OTTO DIELS (*Ber.*, 1921, **54**, [*B*], 213—226).—As a result of previous work (Diels and Paquin, A., 1913, i, 839), the conclusion has been drawn that azodicarboxylic ester is converted by primary and secondary amines into the corresponding substituted amides, whilst with tertiary amines it yields additive compounds such as $NMePh\cdot CH_2\cdot N(CO_2Et)\cdot NH\cdot CO_2Et$. This statement is now found to be too general, since, under suitable conditions, additive compounds can also be formed from primary amines. These substances appear to be divisible into two classes; those formed from aniline and *p*-toluidine, for example, are themselves stable but not capable of further reactions and merely convertible into their components or the transformation products of the latter, whilst that derived from β-naphthylamine is not split up into its components in any of the numerous reactions yet investigated. The latter substance is shown to have the constitution indicated by the annexed formula, since it contains the primary amino-group of β-naphthylamine intact, whilst the hydrazino-group occupies the α-position because the substance



is converted by hydriodic and glacial acetic acids into the anhydrobase obtained by Liebermann and Jacobson by reduction of 1-nitro-2-acetylaminonaphthalene and is transformed by hydrogen peroxide in the presence of glacial acetic acid into a substance which, when warmed, passes into ethyl α-naphth*iso*triazole-1-carboxylate identical with the product obtained from α-naphth*iso*triazole and ethyl chloroformate.

2-*Amino*-1-*dicarbethoxyhydrazinonaphthalene*, colourless, shining leaflets, m. p. 198°, is prepared by the addition of ethyl azodicarboxylate to a solution of β-naphthylamine in warm alcohol; the sparingly soluble hydrochloride is readily hydrolysed by warm water. 2-*Acetylamino*-1-*dicarbethoxyhydrazinonaphthalene* crystallises in colourless needles, m. p. 218—219°. The similarly-prepared additive *compound* from azodicarboxylic ester and α-naphthylamine has m. p. 168° and gives an *acetyl* derivative, m. p. 132°. 2-Amino-1-dicarbethoxyhydrazinonaphthalene loses ethyl alcohol under the influence of hot aqueous potassium hydroxide solution or of piperidine and gives the *compound*, $C_{14}H_{13}O_3N_3$, shining prisms, m. p. about 265° (decomp.), when rapidly heated; when boiled with

aqueous alcoholic potassium hydroxide solution it yields the substance, $C_{10}H_6<\begin{matrix}NH\cdot NH\\ NH\ CO\end{matrix}$, pale brown, bronzy prisms, m. p. about 315—320°, which is also obtained from the product, m. p. 265° (see above), and boiling concentrated alcoholic potassium hydroxide solution. Treatment with glacial acetic acid and hydriodic acid (D 1·96) converts 2-amino-1-dicarbethoxyhydrazinonaphthalene into ethyl iodide and 2-methyl-β-naphthiminazole, $C_{10}H_6<\begin{matrix}-N\\ NH\end{matrix}>CMe$, needles, m. p. 169° (the *hydriodide*, silvery crystals and *hydrochloride*, slender, colourless needles, are described).

2-Amino-1-dicarbethoxyhydrazinonaphthalene can be diazotised, but the corresponding diazonium salt or phenol was not isolated. The most convincing evidence of the presence of the free amino-group is found in its conversion by carbonyl chloride into the corresponding *carbamyl chloride*,

$$CO_2Et\cdot NH\cdot N(CO_2Et)\cdot C_{10}H_6\cdot NH\cdot COCl,$$

leaflets, m. p. about 145°, which is converted by the requisite alcohol into the *methyl* ester, colourless crystals, m. p. 207—208°, or *ethyl* ester, m. p. 154°. The chloride loses hydrogen chloride when heated in the vapour of xylene, giving the *substance*,

$$C_{10}H_6<\begin{matrix}N(CO_2Et)\cdot N\ CO_2Et\\ NH\text{——}CO\end{matrix},$$

m. p. 180—181°, which forms an *additive product* with acetic acid, $C_{17}H_{17}O_5N_3,CH_3\cdot CO_2H$, m. p. 127—128°. Oxidation with hydrogen peroxide transforms 2-amino-1-dicarbethoxyhydrazinonaphthalene into the compound, $C_{10}H_6<\begin{matrix}N(CO_2Et)\\ N(OH)\text{—}\end{matrix}>N\cdot CO_2Et$, brownish-yellow, coarse prisms, m. p. about 96° (decomp.), when rapidly heated, which passes into *ethyl α-naphth*iso*triazole*-1-*carboxylate*, $C_{10}H_6<\begin{matrix}N(CO_2Et)\\ \text{——}N\end{matrix}>N$, pale brown prisms, m. p. 124—125°.

H. W

Action of Cyanogen Derivatives on Oxyhæmoglobin. FRED. VLÈS (*Bull. Soc. Chim. Biol.*, 1920, **2**, 223—238).—The action of a large number of cyanogen derivatives on oxyhæmoglobin was investigated, and the results are summarised in tabular form. J. C. D.

Enzymes. V. Resistance of Ptyalin to the Action of Hydrochloric Acid in the Presence of Starch. D. MAESTRINI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 391—394).—Starch paste protects mixed human saliva from the destructive action of hydrochloric acid, the highest concentration of the latter which the enzyme is able to withstand for three hours without irrecoverable loss of the amylolytic properties being 0·16%. The importance of the substrate for the preservation of the enzymic activity of saliva is hence evident. T. H. P.

Influence of some Organic Bases and their Hydrochlorides on the Activity of Pancreatic Amylase. A. DESGREZ and R. MOOG (*Compt. rend.*, 1921, **172**, 551—553).—The three bases examined were methylamine, trimethylamine, and triethylamine. In all three cases the free base exerted an inhibiting action on pancreatic amylase, whereas the hydrochloride in each case favoured the action of the amylase. That this effect of the hydrochloride is not due to its dissociation and the consequent liberation of hydrochloric acid is shown by the fact that small amounts of hydrochloric acid alone inhibit the action of the enzyme. W. G.

The Influence of Neutral Alkali Salts on Diastatic Enzymes. III. Investigations on Pancreatic Diastase. AMANDUS HAHN and RUDOLF MICHALIK (*Zeitsch. Biol.*, 1921, **73**, 10—18. Compare A., 1920, i, 776).—The optimum H-ion concentration for pancreatic diastase is $P_H = 7·10$ when phosphate buffers are used, and $P_H = 5·50$ when acetate buffers are employed. As in the case of ptyalin, a certain regularity was established in the influence of buffers and neutral salts on the action of pancreas diastase. Experiments point to the probability that the activating action of salts is due to the diminution, and the inhibiting action to the increase in size of the colloidal particles of the enzyme.

S. S. Z.

The Influence of Sodium Fluoride on the Action of Pancreatic Diastase. S. LANG and H. LANG (*Biochem. Zeitsch.*, 1921, **114**, 165—193).—The action of pancreatic diastase is inhibited in the presence of sodium fluoride. The percentage of dextrose thus produced is higher than that of the maltose, which would suggest that the enzyme concerned in the production of maltose from starch is inhibited by the salt, whilst the enzyme which converts maltose into dextrose is accelerated by it. The hydrolysis, however, of maltose by pancreatic diastase is scarcely influenced by sodium fluoride. S. S. Z.

The Use of Different Precipitating Agents in the Preparation of Emulsin from Almonds. M. BRIDEL and R. ARNOLD (*Bull. Soc. Chim. Biol.*, 1920, **2**, 216—222).—If precipitation of emulsin is carried out with alcohol, methyl alcohol, or acetone, and prolonged contact with the precipitating agent is prevented, the resulting enzyme preparations are similar to ordinary emulsin. If, however, prolonged contact with the precipitating medium occurs, the enzyme preparation appears to have lost certain of its properties. J. C. D.

Influence of Heat on the Activity of Salicinase. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1921, **172**, 548—551. Compare A., 1911, i, 99, 592; 1913, i, 1426).—The optimum and maximum temperatures of activity of salicinase, when acting over periods of time varying from one hour to four days, have been determined. In both cases the values vary inversely with

the duration of the experiment, but the optimum temperature, which falls to 30° for a period of thirty-two hours, does not diminish further. The temperature of maximum activity of this enzyme is about 70°, and corresponds with the temperature of instantaneous destruction of the enzyme by heat. W. G.

Action of the Urease from Soja Beans on the Animal Organisms. P. CARNOT, P. GÉRARD, and (MLLE) S. MOISSONNIER (*Ann. Inst. Past.*, 1921, **35**, 1—42).—The results obtained by the authors confirm the observation that urease rapidly and completely decomposes the urea of blood in vitro. In forty-eight hours blood exerts no inhibitory action on the enzyme, but in dilute solutions it shows a protective action which is independent of the inorganic salts and alkalinity of the serum and is not due to a substance thermolabile at 65°.

When urease is injected into the organism it slowly disappears from the blood-stream and is taken up at different rates by certain organs, of which the liver appears to fix the largest amount. The urease was not recovered from the urine.

Acute intoxication produced by intravenous injection of urease in the living organism causes rapid destruction of urea, and the animal dies in two or three hours with increased ammonia in the blood. Subcutaneous injection produces similar results, but more slowly.

The types of intoxication produced resemble those which are obtained by the injection of salts of ammonia and weak acids.

No toxic action was observed after administration of the enzyme by the mouth.

No anti-urease or immunisation against this enzyme was produced, but a substance of the precipitin type was encountered.

J. C. D.

The Properties of Hydroxynitrilase. VERNON K. KRIEBLE and WALTER A. WIELAND (*J. Amer. Chem. Soc.*, 1921, **43**, 164—175).—Further investigations of the conditions governing the formation of mandelonitrile from benzaldehyde and hydrogen cyanide under the influence of hydroxynitrilase (compare Krieble, A., 1913, i, 1255; Rosenthaler, 1909, i, 74; 1913, i, 411, 663). To follow the course of the action in so far as the formation of optically active nitrile was concerned, a portion of the liquid was hydrolysed from time to time by hydrochloric acid and the optically active mandelic acid produced was estimated. The temperature coefficients of the spontaneous reaction of benzaldehyde and hydrogen cyanide and the action in the presence of the enzyme are different. At 0° the enzyme is more efficient, but at 35° the spontaneous action is more rapid. The hydrogen-ion concentration of the medium has, however, a very marked effect on the ratio of spontaneous to enzyme action. In neutral solutions practically all the benzaldehyde and hydrogen cyanide combine spontaneously and almost instantaneously. As the hydrogen-ion concentration is increased the spontaneous action is repressed, and at $P_H = 10^{-5}$ to 10^{-6} the enzyme exhibits its maximum activity.

The phenomenon noticed by Rosenthaler (*loc. cit.*), that the optical activity of the nitrile rises to a maximum and then falls to zero, is explained on the basis that there is only one hydroxynitrilase, namely *d*-hydroxynitrilase, which synthesises only *d*-mandelonitrile, whereas the spontaneous action gives equal amounts of *d*- and *l*-nitrile. As the action is reversible, when the reverse change becomes more marked the excess of *d*-nitrile decomposed becomes greater and the optical activity gradually declines.

W. G.

Phenylacetic-*p*-arsinic Acid. GEORGE ROSS ROBERTSON and JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1921, **43**, 179—181).—*p*-Aminophenylacetic acid is converted into *phenylacetic*-p-*arsonic acid*, $CO_2H\cdot CH_2\cdot C_6H_4\cdot AsO_3H_2$, m. p. 195°, by the Bart reaction (A., 1913, i, 115). When neutralised with alkali and heated with sodium hydrosulphite it gives a light yellow *arseno*-derivative soluble in sodium carbonate. Modifications in the preparation of *p*-nitrophenylacetonitrile, its subsequent hydrolysis, and the reduction of the nitro-compound are described. W. G.

Physiological Chemistry.

Variations in Alveolar Carbon Dioxide Pressure in Relation to Meals. E. C. DODDS (*J. Physiol.*, 1921, **54**, 342—348).—After a meal the alveolar carbon dioxide pressure rises 2—6 mm. in the first half- or three-quarters of an hour, then falls about the same amount below normal, before returning to the original level. The rise is probably connected with gastric, the fall with pancreatic, secretion. In a man from whom the greater part of the stomach had been removed, only the fall occurred.

G. B.

The Carbon Dioxide Absorption Curve and Carbon Dioxide Tension of the Blood of Normal Resting Individuals. JOHN P. PETERS JUN., DAVID P. BARR, and FRANCES D. RULE (*J. Biol. Chem.*, 1921, **45**, 489—536).—The absorption curves of three normal subjects have been determined, and show agreement with those previously reported by earlier observers. The curve of any individual is quite characteristic and remains constant over a considerable period of time. The relationship of the alveolar carbon dioxide to the height of absorption curve and other factors is discussed.

J. C. D.

Agglutination by Ricin. J. A. GUNN (*Proc. Physiol. Soc.*, Dec. 18, 1920; *J. Physiol.*, 1921, **54**, lxxxviii—xc).—Ricin agglutinates, not only blood, but also cholesterol suspensions and other

suspensions of negatively charged particles. The agglutination by ricin is, at least partly, non-specific. The agglutinated particles have lost their charge. G. B.

The Calcium of the Blood. M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1921, **114**, 58—62).—In contradistinction to the observations of Hamburger and Jansen, the author has already pointed out that human blood corpuscles do not contain calcium. Plasma obtained by the application of hirudin shows a higher calcium content than the corresponding serum. The concentration of the free calcium ions in the blood is in progress of investigation. S. S. Z.

The Chemical Composition of Blood Corpuscles. W. FALTA and M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1921, **114**, 145—151).—Data of analyses of various samples of blood from different patients and animals are given. S. S. Z.

Physiology of the Blood Sugar. V. How is the Partition of Dextrose between the Red Corpuscles and the Outside Fluid to be Explained? RICH. EGE (*Biochem. Zeitsch.*, 1921, **114**, 88—110. Compare A., 1920, i, 781).—From osmotic experiments it is found that, in conformity with the observations made by analytical chemical methods, the red corpuscles of the goat, of cattle, and of the rabbit are impermeable to dextrose. Human corpuscles, on the other hand, are permeable to that sugar. The velocity of the diffusion is small; this is most probably due either to combination with or absorption by the membrane of the corpuscles. S. S. Z.

Partition of Cholesterol and its Esters between Blood Corpuscles and Plasma under Physiological and Pathological Conditions. M. RICHTER-QUITTNER (*Wien. Arch. inn. Med.*, 1920, **1**, 425—454; from *Chem. Zentr.*, 1921, i, 340).—Under normal conditions as also in alimentary and, generally, in pathological hypercholesterolæmia, the total cholesterol is absolutely evenly distributed between plasma and corpuscles; occasionally it is somewhat higher in the plasma in the latter circumstances. Under physiological or pathological conditions the presence of cholesteryl esters is not observed in the blood corpuscles of man, horse, ox, dog, cat, or rabbit. Under physiological conditions cholesterol is present entirely as esters in the plasma; small amounts of free cholesterol are also found in cases of pathological hypercholesterolæmia. Administration of fat, of a diet rich in cholesterol or of the latter in the free state causes an increase in the cholesterol content of the blood, both as the free alcohol and its esters. Increased amounts of cholesteryl esters in the plasma are first observed, followed, after some hours, by an equilibrium. A portion of the cholesteryl esters passes from the plasma into the blood corpuscles and is immediately hydrolysed, since the presence of the esters can never be detected in the corpuscles. In the case of pathological hypercholesterolæmia, the free cholesterol is alone increased. H. W.

Are there any Protective Enzymes against the Polysaccharides? E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1921, **114**, 27—32).—The serum of certain animals is normally capable of hydrolysing starch and glycogen, whilst that of other animals does not possess this function normally. The serum of a dog injected with gum arabic and inulin does not hydrolyse these products, and the serum of a rabbit injected with inulin, glycogen, and soluble starch also fails to saccharify any of these substances. The authors therefore cannot confirm Abderhalden's observations of the formation of protective enzymes. S. S. Z.

Physico-chemical Investigations on Body Fluids. II. The Condition of the Sugar in Serum. STEFAN RUSZNYÁK (*Biochem. Zeitsch.*, 1921, **113**, 52—55. Compare this vol., i, 73).—A part of the reducing substances of the blood does not pass through in ultra-filtration through a collodion membrane. The magnitude of this fraction is independent of the sugar content of the blood.

S. S. Z.

Physico-chemical Investigations on Body Fluids. III. The Condition of the Residual Nitrogen. STEFAN RUSZNYÁK and GEZA HETÉNYI (*Biochem. Zeitsch.*, 1921, **113**, 56—57).—The residual nitrogen in the ultra-filtrate of a serum is proportionately higher than that in the corresponding original serum, and lower than that of the residue which has not passed through the filter.

S. S. Z.

Serum Lipochrome. HIJMANS VAN DEN BERGH and P. MULLER (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 766—773).—The lipochrome content of blood serum is determined by precipitating 2 c.c. of serum with 2 c.c. of 96% alcohol, the mixture being centrifuged and the precipitate extracted with 2 c.c. of ether. The extract is compared colorimetrically with a standard colour solution of potassium dichromate. If a large amount of bilirubin is present, the ether extract is washed with a few drops of a very dilute solution of sodium hydroxide before the comparison. The lipochrome content of plants and of animal tissues may be estimated by a slightly modified process.

Examination of various body-tissues and fluids by this method shows that the blood is poorest in lipochrome, the richest being the adrenal. After this generally follows the liver, fat, and spleen. The authors were not able to detect any relationship between specific diseases and the amount of lipochrome in the blood or the tissues. The lipochrome content of the blood rises with a diet rich in lipochrome and falls with one poor in lipochrome. The peculiar diet is responsible for the high values in the case of diabetes. W. G.

The Influence of CO_3-, Cl-, and PO_4-ions on the Oxidation Processes in the Animal Body. RICHARD BING (*Biochem. Zeitsch.*, 1921, **113**, 210—230).—The influence of the above ions

was studied on a dog fed on a basal diet of the same constitution as that used by Mäder. It was found that a deficiency of salts increases the oxidation process in the body when in a resting condition. It was further found that thirteen to twenty-two hours after a meal rich in carbohydrates and deficient in the ions the respiratory quotient was higher than when the above ions were present. On the administration of the ions to a starved animal the respiratory quotient rose definitely. It is assumed that the therapy of alkali springs may be due to this cause. S. S. Z.

Combination of Mineral Salts with Organic Colloids and the Condition in certain Growths. ALBERTO SCALA (*Ann. d'Ig.*, 1920, **30**, 251—273; from *Chem. Zentr.*, 1921, i, 333—334).— The author has shown previously that acid is liberated by the contact of certain neutral salts with colloids, such as gelatin, agar-agar and muscle flesh, in a degree which depends on the nature and the degree of dissociation of the salt and on the properties of the colloid. The phenomenon is attributed to a readier hydrolysis of the amount of the adsorbed salt; if the washing is continued, a neutral and finally an alkaline series of waters are obtained, provided that the base of the salt used is soluble in water; heavy metals are retained by the colloid. The salts of the alkaline earths behave similarly to those of the alkali metals, since their bases are more or less soluble in water. Aluminium behaves as a heavy metal, since its hydroxide does not dissolve. Union with an insoluble kation does not influence the behaviour of gelatin, and possibly of other colloids, towards salts. The mineral salts in the turnip, potato, radish, cucumber, pumpkin, and parsnip are united to the colloid in the same manner as in the artificial mixtures, and behave in an exactly similar manner when treated with water. The compounds are very stable when preserved in an ice-chest, but are irreversibly changed when warmed at 50—70°, so that the acid is very rapidly removed by water. The author considers that undue attention has been paid to the organic components of the extracts in the investigation of accessory food factors, since frequently a very large proportion of the inorganic substances passes into the water, alcohol, and acid. It is readily possible that a gap is produced in the series of necessary inorganic nutrient substances by the one-sided administration of a certain nutriment. Substances of the hydroxypyridine series may also possibly act as carriers for inorganic materials, which they readily adsorb in alcoholic solution. Antiscorbutin shares the slight stability towards heat of the colloidal salt complexes; the acid components which are liberated on heating readily pass into the wash or boiling waters. The residue can lose bases when further washed, but possibly still contains the beriberi vitamin, which is stable in boiling water. The author further considers that decomposition of the colloid–salt complex is possible under the influence of varying physical and psychic stimuli, thus establishing a connexion between the pathology and therapeutics of many diseases, particularly those of the neoplasm. H. W.

Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. VIII. Composition of the Brain in Dementia præcox. GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1921, **113**, 231—245. Compare A., 1914, i, 899).—The chemical examination of brains from patients suffering from dementia præcox has revealed a higher content of water, an almost normal or a slightly more than normal content of cholesterol, a marked diminution in the unsaturated phosphatides which varied from 20—35%, a marked diminution in saturated phosphatides, cerebrosides, and sphingogalactosides, etc., which was of the order of about 50%, and a definite increase in the protein residue. S. S. Z.

The Action of Arrest by the Liver on the Exogenous Uric Acid. CHAUFFARD, P. BRODIN, and GRIGAUT (*Compt. rend.*, 1921, **172**, 477—479).—The authors have determined the uric acid content of the portal and sub-hepatic blood respectively of dogs on different diets. With fasting dogs or dogs on a diet containing only traces of uric acid the values are the same, but where the diet is rich in uric acid, as much as 50% of the uric acid in the portal blood may be retained in the liver, this organ thus regulating uricæmia. This regulating action is periodic and dependent on the diet. W. G.

Investigations on the Cause of the Variations in the Reaction in Normal Human Urine. JULIUS HOLLÓ (*Biochem. Zeitsch.*, 1921, **113**, 246—254).—It was found that on injecting phosphates intravenously they were excreted mostly as acid salts. but on consumption of water the salts were excreted more as alkaline salts. It is concluded that the excretion of acid urine is associated with the tubules and that of the alkaline urine with the glomeruli of the kidney. S. S. Z.

Elimination of Silicic Acid in the Urine after Administration of certain Silicic Acid Preparations. F. ZUCKMAYER (*Ther. Gegen.*, 1920, **61**, 344—350; from *Chem. Zentr.*, 1921, i, 418).—The following preparations were administered: (1) silicic acid infusion from Herba Equiseti, Galeopsidis, and Polygoni, (2) freshly prepared colloidal silicic acid solution, (3) colloidal silicic acid amylodextrin, (4) colloidal silicic acid albumin, and (5) colloidal silicic acid casein metaphosphate. Silicic acid was eliminated most rapidly and in greatest amount after administration of (2) (the values observed with the others are only about half as great) and then from (1) and (4). Simultaneous administration of chalk diminishes the elimination of silicic acid. H. W.

Is there a Specific Action of Bromine Salts? ERNST OPPENHEIMER (*Arch. expt. Path. Pharm.*, 1921, **89**, 29—45).—Benzene extracts of the brains, organs, and other parts rich in lipoids emanating from animals intoxicated with sodium bromide show the presence of small quantities of bromine. Sodium chloride does not react with lipoids in this way. It is suggested that the combination is of a physico-chemical character. S. S. Z.

Colloidal Arsenic (and the Pharmacological Action of Yellow Arsenic). FRITZ KÜLZ (*Arch. Exp. Path. Pharm.*, 1921, **89**, 111—143).—The pharmacological action of colloidal arsenic can only be established when it has undergone oxidation and the general course of the intoxication therefore resembles more or less that of arsenious oxide. Experiments with the object of ascertaining the capacity of colloidal arsenic to induce formation of new blood in anæmia did not yield any consistent results. The action of colloidal arsenic in certain protozoal infections in the mouse was the same as that of arsenious oxide. The results with the yellow modification of arsenic also showed that in the elementary condition the metal has no pharmacological action. S. S. Z.

Physiological Action of ββ′-Di-iodo*iso*propyl Alcohol and of βγ-Di-iodo-*n*-propyl Alcohol. MARIO A. MANCINI (*Arch. Farm. sperim. Sci. aff.*, 1920, **30**, 161—172).—When introduced into the dorsal lymphatic gland of the frog, ββ′-di-iodo*iso*propyl alcohol causes torpor developing into complete muscular paralysis, whilst βγ-di-iodo-*n*-propyl alcohol gives rise to tetanic convulsions, followed by muscular relaxation and death. The action of the latter isomeride appears to be due to the ease with which it decomposes into allyl alcohol and iodine. T. H. P.

The Physiological Action of some Naturally Occurring Hydroxycoumarins (Umbelliferone, Daphnetin, Aesculetin, Chrysatropic Acid, and Herniarin). ERNST SIEBURG (*Biochem. Zeitsch.*, 1921, **113**, 176—199).—The physiological action of the above compounds was studied on fishes, frogs, and rabbits. The influence of the hydroxycoumarins in the presence of light on the diminution and on the increase of the resistance of blood corpuscles to hæmolysis by saponin has also been studied. S. S. Z.

Adrenaline Glycæmia. A. BORNSTEIN (*Biochem. Zeitsch.*, 1921, **114**, 157—164).—Adrenaline increases pulmonary ventilation, diminishes the alveolar tension of carbon dioxide, and furthers the dissipation of the gas; consequently the respiratory quotient increases. Glycæmia which is not due to combustion of carbohydrates is also produced. Adrenaline raises the consumption of oxygen. S. S. Z.

Physiological Action of Optical Isomerides. VII. Hyoscines and Hyoscyamines. ARTHUR R. CUSHNY (*J. Pharm., Expt. Ther.*, 1921, **17**, 41—61. Compare A., 1919, i, 507).—Two hyoscines, each of them racemised in the oscine component, but opposed in the direction of rotation of the tropyl radicle, were examined and it was found that the *l*-hyoscine is fifteen to eighteen times as powerful as the *d*-hyoscine in action on the terminations of the nerves in the salivary glands and in other "specific" atropine effects. *d*-Hyoscine and *d*-hyoscyamine are more slowly destroyed in the tissues than *l*-hyoscine and *l*-hyoscyamine. The action of the hyoscines on nerve-ends in striated muscles, on unstriated muscle, and on the central nervous system is identical.

It is suggested that the "specific" effects of the atropine groups arise from the physical properties of some chemical compound formed with an optically active substance in the tissues, while the less specific effects may be explained by the properties of the uncombined alkaloid. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Micro-organisms on Organic Compounds. II. The Solubility of some Organic Acids in Fatty Oils. P. E. VERKADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 783—789. Compare A., 1920, 1, 916).—An examination of the relative solubilities of cinnamic, salicylic, and benzoic acids in six different fatty oils, and of the coefficient of distribution between oil and water, show that the relation between the solubilities varies with the different oils and is not related in any way to the constitution of the oils. Thus the coefficient of distribution of a substance between olive oil and water cannot constitute any criterion as to the behaviour of the substance towards the living cell (compare Waterman, *Centr. Bakt.*, 1914, **42**, 639). W. G.

Protein Reactions. III. Cataphoresis Experiments with Micro-organisms. A. VON SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1921, **113**, 29—35).—Bacteria travel mostly to the anode, trypanosomes partly to the anode and partly to the cathode in the electric field. No morphological differentiation could be established between the organisms travelling in different directions. The author suggests the possibility of utilising the cataphoretic behaviour of organisms in chemotherapy. S. S. Z.

Protein Reactions. IV. The Physical Chemistry of Agglutination. A. VON SZENT-GYÖRGI (*Biochem. Zeitsch.*, 1921, **113**, 36—41).—The isoelectric point of agglutinins lies between about P_H $2 \cdot 10^{-6}$ and P_H $4 \cdot 10^{-6}$. At higher H-ion concentrations they travel towards the anode, at lower H-ion concentrations towards the cathode in the electric field. Bacteria are fully agglutinated at a H-ion concentration of about P_H 10^{-5}—P_H 10^{-6}, and are not at all agglutinated beyond P_H 10^{-9} and P_H 10^{-2}. On centrifuging bacteria digested with an agglutinating serum for forty minutes, the serum retains its agglutinating potency when the reaction is on the alkaline side of the scale; when it is on the acid side a certain amount of its potency is also retained. It is assumed that the failure to agglutinate by a serum beyond certain H-ion concentrations is due to the deficient combination of the bacteria with the agglutinins. S. S. Z.

Influence of Luminous Radiations on Azotobacter. E. KAYSER (*Compt. rend.*, 1921, **172**, 491—493).—The previous studies (this vol., i, 79, 208) have now been extended to the twelfth generation. In the mannitol medium the total quantity of carbohydrate consumed and the total quantity of nitrogen fixed diminishes with the number of generations. For the twelfth generation a change in the colour of the lighting lessens this diminution. The differences due to colour are still more marked in a medium containing dextrose. W. G.

The Influence of Various Metallic Salts on the Formation of Bacterial Degradation Products from Amino-acids. ICHIRO OTSUKA (*Biochem. Zeitsch.*, 1921, **114**, 81—87).—The addition of metallic salts to a nutrient medium containing Henderson's phosphate mixture and on which *Bacillus proteus* has been grown produces the formation of *d*-*p*-hydroxyphenyl-lactic acid from *l*-tyrosine. Aluminium phosphate is more pronounced in this action than the other salts. The presence of lactic acid in the ordinary medium does not conduce to the production of *d*-*p*-hydroxyphenyl-lactic acid by the action of the metal salts. The function of bacteria for decarboxylising amino-acid deteriorates on cultivation. S. S. Z.

The Formation of *p*-Hydroxyphenylacetic Acid and *p*-Hydroxyphenylacrylic Acid from Tyrosine by Means of Bacterial Action. KINSABURO HIRAI (*Biochem. Zeitsch.*, 1921, **114**, 71—80).—Through the action of *Bacillus proteus vulgaris* tyrosine is converted in Ringer's solution first into *p*-hydroxyphenylacrylic acid and eventually into *p*-hydroxyphenylacetic acid. If glycerol and phosphate salts are used in the medium, *p*-hydroxyphenyl-lactic acid is formed from tyrosine by the same organism. *p*-Methoxycinnamic acid and cinnamic acid were not oxidised to the corresponding acetic acids by the organism in Ringer's solution. S. S. Z.

The Toxicity towards *Staphylococcus* of Dilute Phenol Solutions containing Sodium Benzoate. KENNETH E. BURGESS (*J. Physical Chem.*, 1920, **24**, 738—740).—Determinations of the rate at which *Staphylococcus* is poisoned by dilute solutions of phenol with and without the addition of sodium benzoate confirm the conclusion that the abnormalities observed by Lemon (A., 1920, i, 917) were due to plasmolysis. Addition of methylene-blue and examination under the microscope before pouring the plates saves time in this type of work. W. G.

The Toxicity of Mercuric Chloride and its Solubility in Aqueous Alcohol. J. STANLEY LAIRD (*J. Physical Chem.*, 1920, **24**, 736—737).—Mercuric chloride shows a pronounced minimum of solubility in 24% alcohol, and this corresponds closely with the maximum toxicity in such solutions observed by Paul and Krönig (A., 1897, ii, 155). W. G.

The Nutritional Requirements of Yeast. I. The Rôle of Vitamins in the Growth of Yeast. ELLIS I. FULMER, VICTOR E. NELSON, and F. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1921, **43**, 186—191).—Culture experiments with yeast and alcoholic extracts of lucerne and wheat embryo indicate that these extracts act as growth stimulants to yeast, but that the stimulant is not the water soluble *B*-vitamin. W. G.

The Nutritional Requirements of Yeast. II. The Effect of the Composition of the Medium on the Growth of Yeast. ELLIS I. FULMER, VICTOR E. NELSON, and F. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1921, **43**, 191—199. Compare preceding abstract).—A study of the influence of the nature and concentration of known components of the medium on the growth of yeast. Purely synthetic media containing nothing but inorganic salts and sucrose were used. It was found that yeast grew on a medium free from calcium and magnesium for a period of three months, being transferred every other day, and remained quite normal in its appearance. The optimum concentration of several ammonium salts was identical with that for ammonium chloride. The optimum concentration of ammonium chloride for growth of yeast is the concentration of the salt in which a protein, as measured by wheat gluten, is least swollen. It varies with the temperature. The presence of certain colloids, such as dextrin, appears to favour the growth of yeast. W. G.

The Proteins of Yeast. PIERRE THOMAS (*Ann. Inst. Past.*, 1921, **35**, 43—95).—Two new proteins may be separated from the aqueous extract of yeast (Lebedev), of which one is a true albumin and the other a phosphoprotein. The yields are considerably larger if the operations are performed in a weakly alkaline solution at about 35°. These proteins are present in Buchner's juice and may be coagulated at low temperature. It therefore appears that they are pre-existent in the living yeast-cell.

The phosphoprotein, for which the name *zymocasein* is suggested, is insoluble in water, soluble in alkali hydroxides, and contains 16·15% of nitrogen and 1·80% of phosphorus. Its properties place it between milk caseinogen and egg vitellin. It is clotted by rennet, but less completely than caseinogen.

The albumin, which is termed *cerevisin*, is soluble in water and coagulable at 41°. Several coagulation points may be observed below 70°, but it does not appear to be necessary to assume that several substances are present. It contains 16·35% N and 0·90% S with traces of phosphorus, due probably to impurities. The hydrolysis of zymocasein confirms its resemblance to caseinogen, and the following represent percentages of total nitrogen: ammonia-N, 3·97, humus-N, 9·26; histidine-N, 4·68; arginine-N, 7·56; lysine-N, 5·14; monamino-acids-N, 69·39. By the author's colorimetric estimation for tryptophan it was found to contain 1·51% of that amino-acid.

Cerevisin resembles leguminin of peas, and gave on analysis the

following percentages of total nitrogen: ammonia-N, 3·43; humin-N, 6·22; histidine-N, 3·39; arginine-N, 8·84; lysine-N, 9·64; monamino-acid-N, 68·48.

This protein contains 2·28% of tryptophane, a fact which, together with the high lysine value, indicates that its biological food value would be high. It is well assimilated by the animal organism. J. C. D.

Effect of Alcohol on the Toxicity of Phenol towards Yeast. ELLIS I. FULMER (*J. Physical Chem.*, 1921, **25**, 10—18).—Yeast cells from a wort culture in which the alcohol produced by fermentation has reached a certain concentration are much more resistant to phenol than normal cells. Addition of alcohol to the wort before seeding with yeast brings about the same effect in a shorter time. Methods are described for growing yeast free from these abnormal cells. If inability to grow colonies on wort-agar be taken as the criterion of death, solutions of phenol, water, and 3·75% of alcohol are more toxic than chemically equivalent solutions without alcohol, but if ability to stain with methylene-blue be taken as the criterion they are equally toxic. Immersion in 8% solution of alcohol in water increases the number of cells which stain with methylene-blue; consistently with this, solutions containing phenol, water, and 7·5% of alcohol increase the percentage of stained cells more rapidly than do chemically equivalent solutions of phenol in water. J. R. P.

The Action of Methylene-blue and certain other Dyes on Living and Dead Yeast. CHAS. G. FRASER (*J. Physical Chem.*, 1920, **24**, 741—748).—The dyes examined were Grübler's methylene-blue, magenta, Congo-red, erythrosin, and safranin (water-soluble), Merck's methylene-blue, gentian violet, and methyl-green, and Kahlbaum's methylene-blue *6B* extra. Their behaviour with living yeast and with yeast killed either by boiling or by the action of phenol was examined in order to find a convenient criterion of death in quantitative toxicological investigations with microbes. Erythrosin and methylene-blue *6B* extra gave the best results. In a solution of extract of malt to which methyl-green has been added, yeast-cells may lose their power of reproduction without becoming stained. W. G.

Methylene-blue as Indicator in Determining the Toxicity of Phenol and Phenol-Salt Solutions towards Yeast. CHAS. G. FRASER (*J. Physical Chem.*, 1921, **25**, 1—9. See A., 1920, i, 917).—Solutions containing phenol and sodium chloride of such compositions as to be in equilibrium with the same solution of phenol in toluene or in petroleum are isotoxic towards yeast, if the ability of the cells to stain with methylene-blue be adopted as the criterion of death. If inability to form colonies on wort-agar be adopted as the criterion, the solutions containing salt are more toxic. J. R. P.

Action of Saponin on Vegetable Cells. FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1920, **38**, 350—353).—Saponin considerably increases the rate of fermentation of sugars by yeasts, but the effect is inhibited by the addition of alkali salts. Live yeasts cannot be stained with dyes when saponin is present. Saponin also increases the rate of diffusion of the cell contents of such leaves as those of the red cabbage, fuschia, begonia, etc.

W. P. S.

The Influence of Selenium on the Development of some Moulds belonging to the *Penicillium* Genus. ANTONÍN NĚMEC and VÁCLAV KÁŠ (*Biochem. Zeitsch.*, 1921, **114**, 12—22).—Extremely small quantities of sodium selenite raise the crop of moulds belonging to the *Penicillium* genus even in the presence of manganese and zinc. *Penicillium candidum* is much more sensitive to this stimulating action than *P. roqueforti*. The total ash content in the case of *P. candidum* is increased by the influence of sodium selenite. As the action of the salt becomes toxic the ash content falls. The phosphoric acid content, on the other hand, decreases with the stimulating action of the selenium salt and increases with its toxic influence.

S. S. Z.

Metabolism of Thermophilic Fungi. KURT NOACK (*Jahrb. wiss. Bot.*, 1920, **59**, 413—466; from *Chem. Zentr.*, 1921, i, 414). —The investigations were chiefly effected with *Thermoascus aurantiacus*. Examination of the respiratory metabolism showed that those thermophilic fungi which have a high rate of growth in comparison with other fungi also have an increased metabolism which is not shown by those which grow more slowly. In relationship to temperature, however, the respiratory energy remained lower than was to be expected. Determination of the economic coefficient showed that dextrose, when sole source of carbon nutriment, was decomposed to the extent of 55% in the fungus, whilst 45% was used in metabolic processes. This relationship corresponds with that observed with non-thermophilic fungi, and thus proves that none of the carbon is used directly for the production of heat. The author has shown previously that the vegetative portions of thermophilic fungi have different resistances towards cooling below the minimum temperature of growth (21—35°), and that a species dies the more rapidly as the temperature chosen is lower, the hyphæ being most readily affected. At a constant, sub-minimal temperature, the respiration rapidly diminishes, but the respiratory quotient, $CO_2 : O_2$, remains unaffected by cooling. In contrast to *Aspergillas niger*, *Thermoascus* rapidly adapts itself to chemically different nutriments. Experiments in atmospheres poor in, or free from, oxygen showed that the vegetative mycelium could endure complete withdrawal of oxygen for eight days; under these conditions growth ceases and the respiratory energy is greatly depressed. Re-admission of oxygen causes a marked increase of the respiratory quotient. Respiration, however, is permanently depressed, and only increases through the

growth of new hyphæ; withdrawal of oxygen causes rapid death of the latter. H. W.

A Simple Method of Measuring Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*Science*, 1918, **1217**, 420—422).—Loeb ("Dynamics of Living Matter," 1906, p. 98) has recorded that certain marine algæ on exposure to sunlight cause sea water to become more alkaline. Similar results for fresh-water plants in solutions of hydrogen carbonates were recorded by Czapek (*Biochem. Pflanzen*, 1913, **1**, 519).

Fronds of *Ulva* ("sea lettuce") were enclosed in glass tubes containing sea water. The tubes were immersed in a constant temperature water-bath and exposed to sunlight. Using phenolphthalein as indicator, the change in P_H was followed by matching with the same indicator in a series of buffer solutions. Preliminary experiments showed that the amount of photosynthesis, as measured by the oxygen evolved, was a linear function of the change of P_H and that the presence of indicator was without effect on the process of photosynthesis. Similar experiments were carried out with fresh-water plants in solutions of sodium hydrogen carbonate. For accurate work, precautions must be taken to ensure that no effect on the P_H is produced by the glass of the tubes used. The authors found Pyrex glass to be satisfactory for the purpose. G. W. R.

Differentiation of the Yellow Plant Pigments from the Fat-soluble Vitamin. MARJORY STEPHENSON (*Biochem. J.*, 1920, **14**, 715—720).—The author confirms previous investigators who have shown that the vitamin *A* is not carrotene. The colouring matter of butter may be completely removed by filtration through charcoal without loss of vitamins. J. C. D.

The Presence of Quinic Acid in the Leaves of some Conifers. GEORGES TANRET (*Compt. rend.*, 1921, **172**, 234—236).—Leaves of Cedar of Lebanon gathered in Paris were found to contain 5 grams of quinic acid per kilo. of dried leaves gathered in July, but only 2 grams when the leaves were gathered in December. This acid was also found in larch leaves (*Larix europaea*), but in amounts varying with the place where the trees were growing. It could not be detected in leaves from yew or juniper, or from epicea or fir-tree. The acid as isolated had m. p. 183—184°; $[\alpha]_D$ − 43·2°. Its rotatory power was affected by the addition of ammonium molybdate, first rising to − 63°, then decreasing to − 54·8°, and finally rising again to − 71·7° with increasing amounts of the molybdate. On long keeping in the presence of the molybdate further variations in the rotatory power of the acid were noted. W. G.

The Function of Plant Glucosides. RICHARD WASICKY (*Biochem. Zeitsch.*, 1921, **113**, 1—18).—In the leaves of *Digitalis* the quantity of the glucoside present is dependent on the assimilation. It increases during assimilation and diminishes when the assimilation is interrupted. Both the hydrolysis and the synthesis of the glucosides are attributed to enzyme action. S. S. Z.

The Nitrogenous Compounds in the Egg-plant (*Solanum melongena*, L.). KIYOHISA YOSHIMURA (*J. Chem. Soc. Japan*,* 1921, **42**, 16—22).—The egg-plant contains water, 95·5%, and dry substance, 4·5%, the latter containing total nitrogen, 5·089%, protein nitrogen, 3·710%, and non-protein nitrogen, 1·379%. From a hot water extract there were obtained trigonelline, 0·025%, β-amino-4-ethylglyoxaline, 0·003%, and choline, 0·034%, calculated on the undried substance. K. K.

Constituents of the Corean Ginseng. III. HEISABURÔ KONDÔ and UMETARÔ AMANO (*J. Pharm. Soc. Japan*, 1920, 1024—1043. Compare A., 1915, i, 1087).—A saponin, *panax-saponin*, obtained in an amorphous state from the methyl-alcoholic extract of ginseng, can be hydrolysed by heating for fifteen to sixteen hours with 6% methyl-alcoholic hydrochloric acid. The product of decomposition insoluble in water consists of two substances: (1) *panax-sapogenol*, $C_{27}H_{48}O_3$, colourless prisms, sparingly soluble in ether, m. p. 242·5°, $[\alpha]_D^{19}$ + 20·2°, in 3·3% alcoholic solution, which gives Liebermann's phytosterol reaction and yields a *triacetyl* derivative, m. p. 203°, a *dibromide*, m. p. 187°, and a *dihydro*-compound, m. p. 246°. (2) A light yellow, amorphous powder, easily soluble in ether, m. p. *ca.* 130°, $[\alpha_D^{19}]$ + 23·67°, in 5% alcoholic solution, which also gives Liebermann's phytosterol reaction, and forms a *triacetyl* derivative, m. p. *ca.* 120°, a *dihydro*-compound, m. p. 132°, and a *trichloride*, $C_{27}H_{45}Cl_3$, m. p. *ca.* 135°. This substance may be an isomeride of (1).

The sugars obtained by the decomposition of panax-saponin were dextrose and a pentose. Glycuronic acid was not detected in it. The volatile oil, fatty oil, and glucoside of ginseng produced in Corea and Aizu are essentially identical. K. K.

The Extraction of Glucosides from some Indigenous Orchids; Identification of these Glucosides with Loroglossin. P. DELAUNEY (*Compt. rend.*, 1921, **172**, 471—473. Compare A., 1920, i, 801).—The author has now isolated loroglossin from three other orchids, namely, *Cephalanthera grandiflora* Babingt., *Ophrys apifera*, Huds., and *Orchis bifolia*, L. W. G.

Otoba Butter. WALTER F. BAUGHMAN, GEORGE S. JAMIESON, and DIRK H. BRAUNS (*J. Amer. Chem. Soc.*, 1921, **43**, 199—204).—Otoba butter, the fat expressed from the fruit of *Myristica otoba*, contains the glycerides of myristic, lauric, palmitic, and oleic acids, an essential oil consisting chiefly of sesquiterpenes, and unsaponifiable material which contains otobite and *isootobite*. Otobite apparently contains one methoxy-group, but *iso*otobite does not. They both give *pentabromides*, m. p. 190° and 191° respectively. W. G.

* Previously termed *J. Tokyo Chemical Society*.

Organic Chemistry.

An Improvement in the Nomenclature of Organic Chemistry. T. SHERLOCK WHEELER (*Chem. News*, 1921, **122**, 122—124).—The author suggests a new scheme of nomenclature for organic compounds. J. R. P.

Improved Manufacture of Methane. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Brit. Pat. 146114. Additional to 146110).—In the catalytic reduction of carbon monoxide to methane by means of hydrogen, a product of greater purity, and free from carbon monoxide and hydrogen, is obtained by using carbon dioxide in the later stages of the reaction, when the product contains a high concentration of methane, in the proportion of somewhat more than 1 vol. to every 4 vols. of hydrogen present. Nearly all the hydrogen is thereby converted into methane and water, the latter being periodically separated, whereas with carbon monoxide carbon commences to be deposited when the proportion of hydrogen becomes less than 5 vols. to every vol. of the monoxide present. The excess of carbon dioxide is finally removed from the product by absorption in lime, etc., and traces of hydrogen by passing over heated copper oxide. G. F. M.

Formation of Petroleum from Fish Oils. Origin of Japanese Petroleum. KIUHEI KOBAYASHI (*J. Chem. Ind. Japan*, 1921, **24**, 1—26).—By the distillation of a mixture of herring oil and a finely powdered Japanese acid clay, covered with a layer of the same clay, gases, mainly carbon dioxide, crude oil, and an aqueous liquid were obtained. Amongst the products identified were acraldehyde, soluble fatty acids, such as acetic acid, naphthenic acids, some higher fatty acids, and hydrocarbons. The crude oil had a green fluorescence and a petroleum-like odour, and seemed to be identical with natural crude petroleum. The hydrocarbons in it were principally of the naphthene series accompanied by olefines. The course of the reaction seems to be that the fish oil is hydrolysed to fatty acids and glycerol by the action of water in the clay ($Al_2O_3,6SiO_2,xH_2O$); the glycerol being then converted into acraldehyde, etc., whilst the fatty acids are decomposed into hydrocarbons, partly with formation of acetic and naphthenic acids, but mainly by the elimination of carbon dioxide. The hydrocarbons thus formed will be again cracked to lighter ones by the action of the heated surface of the clay in the upper layer.

From the very close geological relations between the oil fields and the outcrops of Japanese acid clay, and from the results of his experiments, the author considers that the origin of Japanese petroleum

is from a decomposition of marine animals, after putrefaction, under conditions more or less resembling those in the above experiment. K. K.

Preparation of Chloroform from Ethyl Alcohol and the Mechanism of its Reaction. SHUICHIRÔ OCHI (*J. Chem. Ind. Japan*, 1921, **24**, 209—228).—Chloroform is prepared by passing chlorine into a mixture of 10% ethyl alcohol and milk of lime at 60°. The reaction has been examined quantitatively, and from the results the following equations are deduced: (1) $2C_2H_5 \cdot OH + 8CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 5CaCl_2 + Ca(HCO_3)_2 + 2H_2O$, (2) $2C_2H_5 \cdot OH + 10CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + 7CaCl_2 + CaCO_3 + CO_2 + 3H_2O$, (3) $C_2H_5 \cdot OH + 2CaOCl_2 = CH_3 \cdot CO_2H + 2CaCl_2 + H_2O$. Of the formic acid, 65—75% is decomposed into carbon dioxide and water by further oxidation, only about one-fourth remaining undecomposed. About two-thirds of the alcohol is utilised for the formation of chloroform, and of the remainder the greater part is oxidised to acetic acid. Carbon dioxide is not produced directly from alcohol. K. K.

Use of Dichloroethylene as Solvent. ALEXANDER WACKER (*Chem. Zeit.*, 1921, **45**, 266).—As a substitute for ethyl ether, dichloroethylene presents several advantages. Its vapour is not explosive, its solubility in water is only 0·5%, and its affinity for water is negligible, so that drying of the solvent before use is avoided. Its solvent capacity does not materially differ from that of ethyl ether. In the treatment of salt solutions, care must be taken that their specific gravity is not identical with that of dichloroethylene (1·28). W. J. W.

Action of Light on Alcoholic and Acetonic Solutions of Chloropicrin. A. PIUTTI (*Gazzetta*, 1921, **51**, i, 145—146).—Solutions of chloropicrin in alcohol or acetone may be subjected to prolonged boiling in a dark room without change, but when exposed to sunlight, even only for a day, the methyl- and ethyl-alcoholic solutions separate into two layers and deposit crystals of ammonium chloride; the latter also separates from the acetone solution, but this does not form two layers. In these reductions, the carbon and nitrogen of the chloropicrin are parted, whereas in the catalytic hydrogenation of chloropicrin the carbon and nitrogen atoms remain strongly attached; the fate of the $:CCl_2$ residue of the chloropicrin in the former case, and also the nature of the products into which the alcohols and acetone are transformed, are as yet unknown. Various instances of analogous reductions by organic solvents are quoted. T. H. P.

Process for the Purification of Methyl Alcohol. A. LANZENBERG and J. DUCLAUX (*Bull. Soc. chim.*, 1921, [iv], **29**, 135—136).—Commercial methyl alcohol generally contains acetone in addition to other less volatile impurities. It may readily be purified by taking advantage of the fact that methyl alcohol and chloroform

form a eutectic mixture boiling at 53°, whilst with acetone it gives an anti-eutectic mixture boiling at 67°. One part of alcohol is mixed with 7·5 parts of chloroform and the mixture distilled, the fraction boiling at 52·5—53·5° being collected. From this fraction the alcohol is extracted by water and the aqueous alcohol is distilled and rectified in the usual manner. W. G.

Purification and Some Physical Properties of certain Aliphatic Alcohols. ROGER F. BRUNEL, J. L. CRENSHAW, and ELISE TOBIN (*J. Amer. Chem. Soc.*, 1921, **43**, 561—577).—An account of the careful determination of boiling points, densities, and molecular refractivities. Owing to hygroscopicity, satisfactory values for boiling points could be obtained only in presence of drying agents (compare Young and Fortey, T., 1903, **83**, 65; Winkler, A., 1905, i, 850). Of these, aluminium amalgam (Wislicenus and Kaufmann, A., 1895, i, 437, 634) was the most satisfactory, owing to the rapidity of its action; lime and baryta were ultimately equally effective, but metallic calcium, whilst speedy in its action, is not as valuable, possibly owing to the presence of an impurity. The values found are as follows: ethyl alcohol, b. p. 78·32°, D_4^{25} 0·78505, n_D^{25} 1·3595; propyl alcohol, b. p. 97·19°, D_4^{25} 0·7998, n_D^{25} 1·3833. *iso*Propyl alcohol, b. p. 82·26°, D_4^{25} 0·7808, n_D^{25} 1·3749. Butyl alcohol, b. p. 117·71°, D_4^{25} 0·8057, n_D^{25} 1·3974. *iso*Butyl alcohol, b. p. 107·89°, D_4^{25} 0·79801, n_D^{25} 1·3939. *sec.*-Butyl alcohol, b. p. 99·53°, D_4^{25} 0·80271, n_D^{25} 1·39495. Methyl*iso*butylcarbinol, b. p. 131·82°, D_4^{25} 0·8025, n_D^{25} 1·40895. J. K.

Preparation of Alkyl Sulphates. LEON LILIENFELD (Brit. Pat. 143260).—Dialkyl sulphates are prepared from aliphatic alcohols by the direct action of sulphur trioxide in presence of dehydrating agents, and in presence or absence of inert diluents. For example, by passing 80 parts by weight of sulphur trioxide into a well-cooled mixture of 92 parts of absolute alcohol with 400 parts of carbon tetrachloride, then adding 100 parts of anhydrous sodium sulphate and distilling off the carbon tetrachloride, 77 parts of ethyl sulphate were obtained by distillation of the residue in a vacuum and purification of the distillate. Much higher yields are obtainable by using phosphoric oxide as dehydrating agent under suitable conditions. J. H. L.

The Action of Epichlorohydrin on Disodium Hydrogen Phosphate in Aqueous Solution. The Stability of a Monoglyceromonophosphoric Diester. OCTAVE BAILLY (*Compt. rend.*, 1921, **172**, 689—691).—When epichlorohydrin and disodium hydrogen phosphate are mixed in aqueous solution in equimolecular proportion and the solution is allowed to remain, the amount of phosphorus precipitable by magnesia mixture steadily diminishes, and there is a progressive formation of sodium chloride. There is in all probability simultaneous formation of a mixed glycidochloroglycerophosphoric ester and of a monoglyceromonophosphoric diester. If the liquid is boiled for

two hours instead of being kept, almost the sole product is the *diester*, $ONa\cdot PO<^{O\cdot CH_2}_{O\cdot CH_2}>CH\cdot OH$, the intermediate product probably being the chlorohydrin, $PO(ONa)_2\cdot O\cdot C_3H_5Cl\cdot OH$. The stability of this diester in boiling solution is remarkable. W. G.

Perchloromethyl Mercaptan. O. B. HELFRICH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 591—594.—Compare Frankland, Challenger, and Webster, A., 1920, ii, 753).—Perchloromethyl mercaptan is best obtained by chlorinating carbon disulphide at 20—30° in diffused light in presence of 0·3—0·4% iodine until its volume is doubled (compare Rathke, A., 1873, 262, Klason, A., 1887, 1015). Sunlight, a temperature above 30°, and overchlorination favour the formation of carbon tetrachloride, and no other carrier is suitable. The compound, b. p. 149°, 73°/50 mm., is one-third as toxic for dogs, and one-eighth for mice, as carbonyl chloride. On reduction (compare Rathke, *loc. cit.*, Klason, *loc. cit.*) by iron and hydrochloric acid, thiocarbonyl chloride and carbon tetrachloride are obtained, and the latter is the sole product of boiling the compound with iron or zinc fluoride alone. Zinc and hydrochloric acid apparently convert it into methane. J. K.

ββ′-Dichlorodiethyl Disulphide. GEORGE MACDONALD BENNETT (T., 1921, **119**, 418–425).

The Interaction of Sulphur Monochloride and Substituted Ethylenes. WILLIAM JACKSON POPE and JAMES LEONARD BRIERLEY SMITH (T., 1921, **119**, 396—400).

A Sulphide Alcohol, Butylthiolethyl Alcohol. THOMAS COBB WHITNER, JUN., and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 636—638).—β-*Butylthiolethyl alcohol*, $C_4H_9S\cdot CH_2\cdot CH_2\cdot OH$, b. p. 92—93°/3 mm., D_0^0 0·9828, D_{25}^{25} 0·9693, $n_D^{20°}$ 1·4800, from butyl mercaptan and ethylene chlorohydrin in presence of sodium hydroxide, gives an *acetate*, b. p. 84°/4 mm., D_0^0 1·0043, D_{25}^{25} 0·9875, $n_D^{20°}$ 1·4648; a *chloride*, b. p. 68°/6 mm., D_0^0 1·0315, D_{25}^{25} 1·0101, $n_D^{20°}$ 1·4825; and a *bromide*, b. p. 74°/3 mm., D_0^0 1·2308, D_{25}^{25} 1·2089, $n_D^{20°}$ 1·6740. From the last compound, *dibutyl ethylene disulphide*, $C_2H_4(S\cdot C_4H_9)_2$, b. p. 130°/5 mm., is prepared, which is also obtained from ethylene dibromide and butyl mercaptan. *Butyl vinyl sulphide*, $C_4H_9\cdot S\cdot CH\colon CH_2$, is produced by the action of sodium ethoxide on butylthiolethyl bromide, and is converted back into this bromide by treatment with hydrobromic acid. The corresponding iodide could not be obtained in the pure condition. J. K.

Some Derivatives of Butyl Mercaptan and their Mercuric Iodide Compounds. THOMAS COBB WHITNER, JUN., and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 638—642).—The following compounds have been prepared from butyl mercaptan or its sodium salt:

Ethyl butyl sulphide, $C_4H_9\cdot SEt$, b. p. 144—145°, D_0^0 0·8763, D_{25}^{25} 0·8574, $n_D^{20°}$ 1·6527; *mercuroiodide*, $2C_4H_9\cdot SEt,3HgI$, plate, m. p. 163°. *Dibutyl methylene sulphide*, $CH_2(S\cdot C_4H_9)_2$, b. p. 146°/43 mm.,

D_0^0 0·9482, D_{25}^{25} 0·9332, n_D^{20} 1·4964; *mercuri-iodide*, $CH_2(S\cdot C_4H_9)_2,HgI_2$, m. p. 89°; *disulphone*, $CH_2(SO_2\cdot C_4H_9)_2$, m. p. 182°. *Dibutyl ethylene sulphide* (compare preceding abstract), D_0^0 0·9524, D_{25}^{25} 0·9389, n_D^{20} 1·4962; *mercuri-iodide*, $C_2H_4(S\cdot C_4H_9)_2,HgI_2$, m. p. 85°; *disulphone*, $C_2H_4(SO_2\cdot C_4H_9)_2$, m. p. 180°. *Ethoxymethyl butyl sulphide*, $OEt\cdot CH_2\cdot S\cdot C_4H_9$, b. p. 179—181°, D_0^0 0·9054, D_{25}^{25} 0·8877, n_D^{20} 1·4502, with mercuric iodide gives the *compound*, $OEt\cdot CH_2\cdot S\cdot C_4H_9,2HgI$, m. p. 156°. *Phenacyl butyl sulphide*, $COPh\cdot CH_2\cdot S\cdot C_4H_9$, b. p. 140°/3 mm., D_0^0 1·0712, D_{25}^{25} 1·0589, n_D^{20} 1·5050, *mercuroiodide* (2HgI), m. p. 158°. *Dibutyl ethylidene sulphide*, $CH_3\cdot CH(S\cdot C_4H_9)_2$, b. p. 105°/3 mm., D_0^0 0·9399, D_{25}^{25} 0·9272, n_D^{20} 1·4900, *mercuroiodide* (4HgI), m. p. 138°; *disulphone*, $CHMe(SO_2\cdot C_4H_9)_2$, m. p. 64°. *Dibutyl*iso*propylidene sulphide*, $CMe_2(S\cdot C_4H_9)_2$, b. p. 110°/4 mm., D_0^0 0·9304, D_{25}^{25} 0·9215, n_D^{20} 1·4842, *mercuroiodide* (4HgI), m. p. 159°. *Benzylidene dibutyl sulphide*, $CHPh(SC_4H_9)_2$, b. p. 167°/4 mm., D_0^0 1·0180, D_{25}^{25} 0·9999, n_D^{20} 1·4445; *mercuroiodide* (4HgI), m. p. 86°; *disulphone*, $CHPh(SO_2\cdot C_4H_9)_2$, m. p. 86°. *Phenylethylidene dibutyl sulphide*, $CMePh(S\cdot C_4H_9)_2$, b. p. 167—168°/3 mm., D_0^0 1·0241, D_{25}^{25} 1·0110, n_D^{20} 1·5535; *mercuroiodide* $(HgI)_4$, m. p. 155°. J. K.

The Reaction between Acid Haloids and Aldehydes. III. L. H. Ulich and Roger Adams (*J. Amer. Chem. Soc.*, 1921, **43**, 660—667. Compare this vol., i, 342).—Aliphatic acid haloids and aliphatic aldehydes condense in the same manner as aromatic compounds, reaction being completed by the aid of heat and addition of a small quantity of zinc chloride. Acid bromides react very readily, but form less stable products than the chlorides; the velocity of reaction diminishes slightly with increase of molecular weight, and the products then gradually darken and decompose. They are less stable towards water than the purely aromatic compounds, and decompose in the same manner; those formed from benzoyl chloride and aliphatic aldehydes are the most stable of the three classes, being only slowly decomposed even by dilute sodium carbonate solution. The action of ammonia and primary and secondary aliphatic amines on the new compounds corresponds with that already observed for purely aromatic compounds, but the action of aniline is analogous to that of primary aliphatic bases. Hitherto only tarry products have been obtained from aromatic aldehydes and aliphatic acid haloids. The products from benzoyl chloride and higher aliphatic aldehydes are obtained only after some boiling and are accompanied by aromatic acids and alkylidene dibenzoates, a reaction which is explained by the assumption of an intermediate aldol condensation, followed by elimination of the elements of water. In addition to products already known (Franchimont, A., 1883, 452; Rübencamp, A., 1885, 136; Descudé, A., 1903, i, 735) the following are described: *α-chloro*iso*butyl acetate*, b. p. 78—81°/50 mm.; *α-chloro*iso*butyl propionate*, b. p. 67—70°/18 mm.; *α-chloro*iso*butyl* n-*butyrate*, b. p. 74—76°/10 mm.; *α-chloro*iso*butyl* n-*valerate*, b. p. 80—83°/8 mm.; *α-chloro*iso*valeryl acetate*, b. p. 89—92°/60 mm.; *α-chloro*-n-*heptyl acetate*, b. p. 104—105°/15 mm.; *α-chloro*-n-*heptyl* n-*butyrate*, b. p. 120—122°/15 mm.; *chloromethyl chloroacetate*, b. p. 130—132°/745 mm.; *α-bromoethyl*

acetate, b. p. 122—125°/738 mm.; α-*bromo*iso*butyl acetate*, b. p. 73—75°/30 mm.; α-*bromo*iso*amyl acetate*, b. p. 85—88°/25 mm.; α-*bromo*-n-*heptyl acetate*, b. p. 113—116°/15 mm.; α-*bromoethyl bromoacetate*, b. p. 95—97°/8 mm.; α-*chloroethyl benzoate*, b. p. 120°/8 mm.; α-*chloro*-n-*butyl benzoate*, b. p. 135—138°/18 mm.; α-*chloro*iso*amyl benzoate*, b. p. 145—147°/18 mm.; α-*chloro*-n-*heptyl benzoate*, b. p. 180—183°/18 mm. (compare Lees, T., 1903, 145); *chloromethyl* p-*chlorobenzoate*, b. p. 163—165°/20 mm.; *bromoethyl benzoate*, b. p. 135—137°/19 mm.

Pyridine gives an additive *compound* with chloromethyl benzoate, $C_{13}H_{12}O_2NCl$, m. p. 177—178°, but not with α-chloro-*n*-heptyl acetate, α-chloroethyl benzoate, α-chloro*iso*amyl benzoate, or α-chloro-*n*-heptyl benzoate. Chloromethyl acetate and quinoline yield the *compound*, $C_{12}H_{12}O_2NCl$, m. p. 214—216° (decomp.).

J. K.

The Mixed Anhydrides of Sulphuric Acid and Carboxylic Acids. I. Acetylsulphuric Acid. A. J. van Peski (*Rec. trav. chim.*, 1921, **40**, 103—118).—Acetylsulphuric acid is formed when sulphuric anhydride acts on acetic acid below 0°. This acid reacts with anhydrous sodium acetate to give sodium acetylsulphate, which on heating is decomposed, giving sodium pyrosulphate and acetic anhydride. If, however, the sodium salt is heated with acetic acid, the reversible action

$$CH_3\cdot CO\cdot NaSO_4 + CH_3\cdot CO_2H \rightleftharpoons (CH_3\cdot CO)_2O + NaHSO_4$$

occurs. When heated at 70°, acetylsulphuric acid is converted for the most part into sulphoacetic acid, but a portion of this acid is acetylated by the acetylsulphuric acid still present and converted into acetylsulphoacetic acid, which in part condenses to give *disulphodehydroacetic acid*, $\frac{CH_3\cdot CO}{SO_3H}\!\!>\!C\!<\!\!\frac{CO\cdot O\cdot CMe}{CO\text{——————}}\!\!>\!C\cdot SO_3H$, isolated as its *barium* salt.

Acetylsulphuric acid forms a suitable reagent for acetylating substances such as tribromophenol and tribromoaniline, which ordinarily can only be acetylated with difficulty. With amyl alcohol, however, the product is almost exclusively amylsulphuric acid, whilst phenol gives phenyl acetate and probably phenylsulphuric acid. Acetylsulphuric acid may also act as a sulphonating agent, and with benzene it gives benzenesulphonic acid. W. G.

Catalytic Hydrogenation of Cottonseed Oil. Louis Kahlenberg and George J. Ritter (*J. Physical Chem.*, 1921, **25**, 89—114).—Nickel is the most efficient common metal catalyst for the hydrogenation of cottonseed oil. A catalyst composed of equal parts of nickel and cobalt was more active than either metal alone. Two new varieties of nickel catalysts were prepared, the first by deposition of nickel from solution on zinc and the second by reduction of nickel chloride by hydrogen at 180—250°. Zinc carbonate freshly precipitated in the presence of suspended powdered aluminum and reduced at 350—504°, and bismuth precipitated on charcoal and reduced by hydrogen at 350°, are also fairly active catalysts.

J. R. P.

Constitution of Linolic Acid. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1921, **42**, 130—141).—From the products of oxidation of linolic acid (b. p. 230—231°/16 mm.), with 4% potassium permanganate in alkaline solution, tetrahydroxystearic, azelaic, *n*-butyric, and glutaric acids were isolated. By ozonisation, linolic acid gave a stable diozonide, the decomposition of which by boiling with water produced *n*-butyric acid, *n*-butaldehyde, glutaric acid, glutarodialdehyde, azelaic acid, and azelaicsemialdehyde. The author assigns the constitution,

$$\mathrm{CHMe{\cdot}CH_2{\cdot}\underset{\displaystyle O{\cdot}}{CH}{-}\underset{\displaystyle O{\cdot}O}{CH}{\cdot}[CH_2]_3{\cdot}\underset{\displaystyle O{\cdot}}{CH}{-}\underset{\displaystyle O{\cdot}O}{CH}{\cdot}[CH_2]_7{\cdot}CO_2H},$$

to the ozonide, and $\mathrm{CHMe{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_3{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H}$ to linolic acid. K. K.

Spontaneous Decomposition of Linoxyn. FELIX FRITZ (*Chem. Umschau*, 1921, **28**, 29—30).—The author considers that linoxyn undergoes in the course of time a spontaneous decomposition, becoming viscous and soluble in alcohol, whilst at the same time fatty acids soluble in water are produced, and that this decomposition takes place independently of the presence or absence of air, as, for example, under water, or in the interior of masses of the material where it would be quite impossible for oxidation processes to occur. G. F. M.

The Chemistry of the Glutaconic Acids. XII. The Simultaneous Occurrence of 1 : 2- and of 1 : 3-Addition to "Nascent" Glutaconic Ester. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (T., 1921, **119**, 492—501).

Methyl Tartronate. HARRY LINN FISHER and HAROLD LESTER SIMONS (*J. Amer. Chem. Soc.*, 1921, **43**, 628).—The yield of tartronic acid (Behrend and Osten, A., 1906, i, 229) is tripled if the time of reaction between tartaric acid, fuming nitric acid, and phosphoric oxide is prolonged to twenty-one days. *Methyl tartronate*, $C_5H_8O_5$, m. p. 53·3—53·5° (corr.), from the silver salt and methyl iodide, has a remarkable tendency to sublimation, a fact which is considered to explain failure of the attempt to prepare it by esterification of the acid with hydrogen chloride. J. K.

Nitrotartaric Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 577—581).—Nitrotartaric acid, of which the preparation is detailed, is stable at the boiling point of xylene after careful dehydration over lime or sodium hydroxide, but slowly decomposes in presence of water into nitrous and dihydroxytartaric acids, with some tartronic and oxalic acids, whilst the last two are the only organic acids produced in presence of alkali. It is suggested that these reactions are not due to methylene dissociation (Nef, A., 1900, i, 4), but to a pseudo-form of the acid,

$$\mathrm{CO_2H{\cdot}C(OH)(ONO){\cdot}C(OH)(ONO){\cdot}CO_2H}.$$

The acid itself is the dinitrate of tartaric acid,

$$\mathrm{CO_2H{\cdot}CH(ONO_2){\cdot}CH(ONO_2){\cdot}CO_2H},$$

since it yields this and nitric acid on hydrolysis at the ordinary temperature by concentrated hydrochloric acid, or by moderately dilute sulphuric or nitric acid. J. K.

Derivatives of Acetylenediacetal. A. WOHL and K. JASCHINOWSKI (*Ber.*, 1921, **54**, [*B*], 472—475).—The possibilities of acetylenedialdehyde tetraethylacetal, $CH(OEt)_2{\cdot}C{:}C{\cdot}CH(OEt)_2$ (A., 1912, i, 161), as initial material in the preparation of derivatives of succindialdehyde have been investigated, but the results are disappointing, since the accumulation of diethoxyethyl groups strongly inhibits the addition of reagents at the treble bond. In spite of many variations in the experimental conditions, the substance could not be caused to react with water, alcohol, ammonia, hypochlorous acid, phenylhydrazine, or semicarbazide; with hydroxylamine, however, it gives the additive *product* $CH(OEt)_2{\cdot}C(NH{\cdot}OH){:}CH{\cdot}CH(OEt)_2$, colourless, viscous liquid, b. p. 109—110°/0·02 mm., which immediately decolorises permanganate and bromine, reduces ammoniacal silver solution, but not Fehling's solution, and does not give crystalline compounds with gold or platinum chlorides. The substance is reduced by hydrogen under pressure and in the presence of palladinised animal charcoal at 117° to an *amino*-compound, apparently having the formula $CH(OEt)_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CH(OEt)_2$, yellow liquid, b. p. 107°/0·01 mm., which does not yield crystalline products with gold or platinum chloride; the yield, however, is poor, and the material very difficult to purify. The apparatus used for effecting hydrogenations of this type is fully described and illustrated in the original. H. W.

New Observation on the Chemistry of the Sugars. I. H. KILIANI (*Ber.*, 1921, **54**, [*B*], 456—472).—Experiments, undertaken with the immediate object of preparing free aldehyde acids of the sugar group (or their lactones) have shown that the action of nitric acid at the ordinary temperature is capable of very wide application in the series, and many examples of its use are given.

The substance is treated with a slight excess of nitric acid, which generally has D 1·2 (32% HNO_3); in certain cases a more concentrated acid is used and, if a dilute acid is chosen for any particular reason and fails to react within about twenty-four hours, oxidation can be started by the addition of a small quantity of fuming acid (as a maximum 5% by volume) which operates by the production of nitrous acid. If, in difficult instances, an acid particularly rich in nitrous acid is necessary, it may be prepared by mixing suitable quantities of fuming nitric acid and water (both pre-cooled in ice) at the moment they are required. In every case it is important that the ordinary temperature should be maintained throughout the entire operation. This is best effected by immersing the reaction vessel in a sufficiently large volume of water; cooling with running water or with ice is to be avoided. In spite of the use of calculated quantities of acid, more fully oxidised products are frequently encountered, thus indicating a regeneration of the acid by atmospheric oxidation of the evolved oxides of nitrogen and the advis-

ability of excluding air. The following types of reaction are illustrated:

(i) Oxidation of the majority of the aldoses to the corresponding monobasic acids. *l*-Arabinose gives *l*-arabonic acid (yield 59·2%), *l*-xylose yields *b*-xylonic acid (the salt $C_5H_9O_6 \cdot CdBr$ contains $4H_2O$), rhamnose, which is attacked with difficulty, is converted into the lactone of rhamnonic acid, *d*-galactose gives mucic and *d*-galactonic acids. The behaviour of dextrose is abnormal and not completely elucidated; a very labile intermediate oxidation product appears to be formed, but, if rise in temperature is avoided throughout all operations, from the product crystals, presumably of calcium glycuronate, $(C_6H_9O_7)_2Ca,2H_2O$ (which has been described previously as amorphous), can be prepared. (ii) The separation of aldoses from ketoses. Sorbose and *d*-fructose (and hence probably all ketoses) are unaffected by nitric acid (D 1·2, 32% HNO_3) at the ordinary temperature. (iii) Simple method of preparing lævulose from sucrose. The latter is first inverted by nitric acid and the dextrose converted into an acid separable as the barium salt. (iv) A smooth method of treatment of mixtures of sugars obtained by the hydrolysis of glucosides. The possibilities in the directions (iii) and (iv) depend on the course of the further investigation of the abnormal behaviour of dextrose. (v) A new method of investigating the glucosides themselves as indicated with great probability by preliminary experiments with digitoxin and antiarin. (vi) A new and greatly simplified method of preparing the dibasic acids of the sugar group. Metasaccharin gives calcium trihydroxyadipate in 42% yield; *l*-mannonic acid is converted into the lactone of *l*-mannosaccharic acid in 52·8% yield. (vii) An excellent method for the preparation of glyceric and tartronic acids and probably also of glyceraldehyde from glycerol. (viii) The oxidation (and in many cases the nitration) of organic substances which are attacked by nitric acid of any concentration at the ordinary temperature. Castor oil is converted into azelaic and, apparently, suberic acids, but the identity of the latter is not completely established. Cinnamic and benzoic acids give mainly *m*-nitrobenzoic acid. H. W.

Syntheses of Aliphatic Acyl Derivatives of the Sugar Group. I. KURT HESS and ERNST MESSMER (*Ber.*, 1921, **54**, [*B*], 499—523).—The preparation of acyl compounds of the sugars and the higher fatty acids has been undertaken with the object of studying the properties of molecules which have an analogous structure to the celluxose of cellulose (A., 1920, i, 533). This can be readily accomplished by the action of the requisite acid chloride and sugar dissolved in a mixture of pyridine and chloroform at $-15°$ or, alternatively, by the use of the acid anhydride (compare Behrend and Roth, A., 1904, i, 716). In general, the two methods do not yield identical products and, whilst the latter gives undoubted α-derivatives, the substances obtained from the acid chlorides do not appear to be the β-compounds, but are probably derived from some variety of dextrose other than the γ-oxide form. The esters, up to and including dextrose pentahexoate, are distillable liquids;

the products from the still higher acids are crystalline solids with a fat-like nature and a comparatively low melting point, which approximates to that of the parent fatty acid. With increasing molecular weight, the specific rotation of the esters (the observations recorded were all made in chloroform solution) diminishes, and this observation is of peculiar interest in its bearing on the apparent optical inactivity of cellulose.

[In part with E. A. KLETZL.]—α-Glucose penta-acetate, m. p. 111—112° (identical with the product obtained by Behrend and Roth's method), is prepared by the very gradual addition of a solution of acetyl chloride in chloroform to a suspension of anhydrous dextrose in a mixture of dry pyridine and chloroform at − 10° to − 15°. If the pyridine is replaced by quinoline, an *additive product*, $C_{25}H_{29}O_{11}N,0{\cdot}5H_2O$ is obtained. *Pentapropionyl*iso*glucose* (the term *iso* is applied to the derivatives obtained by aid of the acid chlorides) is a colourless liquid, b. p. 193—195°/1 mm., $[\alpha]_D^{16}$ + 80·87°, whereas *α-glucose pentapropionate* has b. p. 205°/2 mm., $[\alpha]_D^{16}$ + 61·06°. *Pentabutyryl*iso*glucose* and *α-glucose pentabutyrate* have b. p. 215—220°/2 mm., $[\alpha]_D^{16}$ + 73·31° and b. p. 228—230°/1·5 mm., and $[\alpha]_D^{16}$ + 52·04° respectively, whilst *penta*iso*valeryl*iso*glucose* and *α-glucose penta*iso*valerate* have b. p. 242°/2 mm., m. p. about 43° (long needles), $[\alpha]_D^{16}$ + 75·19° and b. p. 242°/3 mm., $[\alpha]_D^{16}$ + 43·68°. *α-Glucose pentahexoate* is a pale yellow liquid, b. p. 240—245°/0·01 mm., $[\alpha]_D^{16}$ + 44·28°, the same product being obtained by either method. The following esters are prepared from the acid chlorides: *α-glucose pentapalmitate*, colourless, plastic mass, m. p. 65—67°, $[\alpha]_D^{16}$ + 34·30°, the solubility of which in various solvents is closely similar to that of tripalmitin; *α-glucose pentastearate*, colourless, crystalline mass, m. p. 70—71°, $[\alpha]_D^{16}$ + 34·17°; *β-monostearyltetra-acetylglucose*, from acetobromoglucose and silver stearate in xylene solution, m. p. 78°; *α-glucose pentaoleate*, slightly discoloured, relatively mobile liquid which could not be distilled without decomposition under 1—2 mm. pressure, $[\alpha]_D^{16}$ + 27·51°; *sucrose octapalmitate*, soft, granular mass, m. p. 54—55°, $[\alpha]_D^{16}$ + 17·12°; *sucrose octastearate*, m. p. 57°, $[\alpha]_D^{16}$ + 16·55°; *raffinose hendekapalmitate*, yellow, waxy mass, m. p. 43° after softening at 39°, $[\alpha]_D^{16}$ + 4·15°; *raffinose hendekastearate*, m. p. 63° (specimens prepared at the ordinary temperature after initial cooling had m. p. 47°, $[\alpha]_D^{16}$ + 27·17° and $[\alpha]_D^{16}$ + 10·02° respectively).

Working on the hypothesis that compounds of the amino-acids and sugars may be of considerable importance in the chemistry of the proteins, the authors have prepared *glucose pentahippurate*, $C_{51}H_{47}O_{16}N_5,2H_2O$, $[\alpha]_D^{16}$ about + 9·8°, by the action of hippuryl chloride on glucose in the presence of pyridine and chloroform.

H. W.

The Hydrolysis of α-Methyl *d*-Mannoside by Soluble Ferments. H. HÉRISSEY (*Compt. rend.*, 1921, **172**, 766—768).—The most satisfactory source of α-*d*-mannosidase is the germinated seeds of lucerne. Emulsin from almonds and dry brewer's yeast exert but a feeble hydrolysing action on α-methyl *d*-mannoside. W. G.

The Unsaturated Products of Reduction of the Sugars and their Transformations. I. The Glucal Problem. MAX BERGMANN and HERBERT SCHOTTE (*Ber.*, 1921, **54**, [*B*], 440—455).—The elucidation of the constitution of glucal triacetate (Fischer, Bergmann, and Schotte, A., 1920, i, 420) has made the structure $OH\cdot CH_2\cdot CH(OH)\cdot\underbrace{CH\cdot CH(OH)\cdot CH{:}CH}_{O}$ highly probable for the parent substance (compare A., 1913, i, 445; 1914, i, 252); this formula can only with difficulty explain the aldehydic properties of the compound. In order to ascertain to what degree unsaturated furan derivatives can exhibit aldehydic characteristics, the authors have investigated the analogous but crystalline rhamnal, which, however, is found to be very stable towards alkalis and unaffected by silver solution or Fehling's solution. Since, therefore, the structural consideration of glucal as a derivative of 2 : 3-dihydrofuran is insufficient to account for the aldehydic properties of previous preparations, glucal itself has been prepared in a modified manner and in a purer condition; in this state it does not show the reactions of an aldehyde. (The terms, glucal, lactal, cellobial, etc., are thus deprived of their original meaning, but a change in nomenclature is not immediately suggested, as it has passed into general use.) It has further been found possible to identify one of the reducing constituents of ordinary glucal preparations as 2-deoxyglucose $OH\cdot CH_2\cdot CH(OH)\cdot\underbrace{CH\cdot CH(OH)\cdot CH_2\cdot CH}_{O}\cdot OH$.

Rhamnal diacetate, $\underbrace{CH{:}CH\cdot CH(OAc)\cdot CH}_{O}\cdot CHMe\cdot OAc$, colourless, viscous liquid, $[\alpha]_D^{20}+63\cdot4^{\circ}$ in *s*-tetrachloroethane solution, is prepared by the reduction of acetobromorhamnose (this vol., i, 94) by zinc and acetic acid at 0° and is purified from admixed β-triacetylrhamnose by distillation under greatly reduced pressure. It is converted by aqueous barium hydroxide solution into *rhamnal*, $\underbrace{CH{:}CH\cdot CH(OH)\cdot CH}_{O}\cdot CHMe\cdot OH$, long, colourless needles, flat prisms, m. p. 74—75°, after slight softening at 71°, $[\alpha]_D^{18}+45\cdot3^{\circ}$ in aqueous solution. The latter is oxidised by perbenzoic acid in glacial acetic acid solution at 0° to rhamnose (yield 75% of that theoretically possible), m. p. 85—92°, $[\alpha]_D^{20}+7\cdot94^{\circ}$ in aqueous solution (final value).

Crystalline glucal is most conveniently prepared by hydrolysing glucal triacetate with absolute methyl alcoholic ammonia; the solution is evaporated and the acetamide separated from the residue by sublimation in a high vacuum at an elevated temperature; the residual product of the reaction is very pure, and can be further crystallised, although with considerable difficulty, from ethyl chloroacetate. It forms needles or more complex aggregates, m. p. about 60°, to a colourless syrup filled with leaflets, $[\alpha]_D^{19}-7\cdot2^{\circ}$ in aqueous solution (for a specimen which had not been recrystallised). Oxidation with perbenzoic acid transforms glucal into mannose (yield 81% of that theoretically possible) which is identified as mannosephenylhydrazone, m. p. 197—201°, $[\alpha]_D^{21}+27\cdot3^{\circ}$, in dry pyridine.

A specimen of glucal which had been prepared by the original process of hydrolysis of glucal triacetate with barium hydroxide solution and showed marked aldehydic properties yielded with *as*-phenylbenzylhydrazine a crystalline product, long needles, m. p. 157—158°, when rapidly heated, $[\alpha]_D^{15} + 7{\cdot}7°$, in methyl alcoholic solution which was identified as 2-*deoxyglucosephenylbenzylhydrazone*; it gave a *tetra-acetate*, colourless crystals, m. p. 113—114°, $[\alpha]_D^{23} + 35{\cdot}35$, in *s*-tetrachloroethane solution. For purposes of comparison, 2-deoxyglucose was prepared by the hydrolysis of 2-deoxymethylglucoside acetate by $N/10$-hydrochloric acid which was then directly converted into the phenylbenzylhydrazone, m. p. 157—158°, $[\alpha]_D^{15} + 8{\cdot}1°$, in methyl alcoholic solution (tetra-acetate, m. p. 113—114°, $[\alpha]_D^{25} + 35{\cdot}2$ in *s*-tetrachloroethane). H. W.

Röntgen-Spectrographic Observations on Cellulose. R. O. Herzog and Willi Jancke (*Zeitsch. Physik*, 1920, **3**, 196—198).—Using the radiation from a Coolidge tube with a copper anticathode, rods made of compressed powders of cotton (ash, 0·03%), ramie (ash, 0·03%), wood cellulose (ash, 0·1%), artificial silk (0·02%), and viscose were examined. It is shown that all exhibit interference figures which are characteristic of a crystalline structure; similar interference is also shown by various varieties of starch. J. F. S.

Action of Hydrazines on Cellulose Acetates. W. Leigh Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 61—63T).—Acetylcellulosephenylhydrazones and acetylcellulose-*p*-bromophenylhydrazones were obtained by treating solutions of various acetylcelluloses with the hydrazines, under different conditions of temperature, time of treatment, etc., followed by removal of the solvent and purification of the product by repeated solution, precipitation, filtration, and washing. The triacetylcellulosephenylhydrazones had m. p. 229—265°, whilst the *p*-bromophenylhydrazones had m. p. 243—287°. These results and the nitrogen content of the substances indicate the manner in which the complex cellulose is degraded into simpler groups of the same empirical composition. W. P. S.

Differentiation between Oxycellulose and Hydrocellulose by Titration. Karl G. Schwalbe and Ernst Becker (*Ber.*, 1921, **54**, [*B*], 545—550).—The differentiation of hydro- from oxycelluloses can be effected with some degree of accuracy by taking advantage of the fact that the latter is the more acidic in character owing to the retention of insoluble or sparingly soluble acids of high molecular weight by the fibre (the simple acids such as formic, acetic, and oxalic, naturally pass into the wash waters).

The experiments were carried out with a bleaching powder oxycellulose from cotton and from cellulose for nitration, a permanganate and a hydrogen peroxide oxycellulose from cotton. The air-dried material (1 gram) was mixed with water (50 c.c.) and titrated with $N/100$-sodium hydroxide. Litmus or phenol-

phthalein (at 80°) was used as indicator, the results being similar, but the end-point rather sharper with the latter. The titration does not proceed very smoothly by reason of the sparing solubility of the acids, but is complete within a few hours. With bleaching powder oxycelluloses a very slight acidity was directly observed, which, however, was found to be due to the fact that the acids were largely present in the form of their calcium salts; when the material was incinerated and the alkalinity of the ash added to the observed acidity, the expected values were obtained. It is thus shown that the total acidity of the oxycelluloses is very considerably higher than that of the hydrocelluloses or of the original materials. The presence of oxycellulose in overbleached cellulose was readily demonstrated in a similar manner.

Hydro- and oxy-celluloses may be readily qualitatively distinguished by mixing the preparations with distilled water and adding a drop of methyl-orange. The liquid is coloured yellow in nearly all cases, but is reddish-orange with certain oxycelluloses. A few c.c. of concentrated sodium chloride solution are now added, which leaves the colour of the hydrocellulose or cellulose suspension almost or entirely unchanged, but gives a wine-red colour to the oxycellulose preparations. The method may be made quantitative by titrating back with *N*/100-sodium hydroxide solution; methyl-red, however, should be used as indicator, since the end-point with methyl-orange is indistinct. H. W.

Lignin and the Sulphite Boiling Process. WALTER FUCHS (*Ber.*, 1921, **54**, [*B*], 484—490).—The recent publications of Klason on this subject (A., 1920, i, 474, 821) have induced the author to make a critical survey of the present state of knowledge. He is led to the conclusion that it is premature to put forward a constitutional formula for lignin. Up to the present it has only been shown definitely that the lignin substances are not homogeneous and that their complexity is probably analogous to that of the proteins or carbohydrates of high molecular weight. Phenols are certainly present in them. They contain methoxyl, hydroxyl, acetyl, and carbonyl groups, and also double bonds. Very little is known of the main portion of the lignin molecule and of its structural relationships.

The sulphite treatment includes at least two separate processes, namely, the detachment of the lignin substance from its natural form of combination in the wood and its subsequent conversion, possibly after further transformations, into soluble sulphur compounds. The nature of the former process is quite uncertain, since nothing is definitely known concerning the mode of union or admixture of cellulose and lignin. The second process may depend on the addition of sulphurous acid at the double bond, to the carbonyl group, or to the phenolic hydroxyl group; further, the possibility must be taken into account that the phenolic nuclei may behave in the sulphide process in their tautomeric form and therefore as unsaturated cyclic ketones (compare Fuchs, A., 1920, i, 159, 545). H. W.

Polysaccharides. II. Constitution of Diamylose. P. KARRER and C. NAGELI (*Helv. Chim. Acta*, 1921, **4**, 169—173. Compare A., 1920, i, 820).—When treated for five days with acetyl bromide at the ordinary temperature, α-tetra-amylose (Pringsheim and Langhans, A., 1912, i, 832; Pringsheim and Eissler, A., 1913, i, 1156) is transformed quantitatively into acetobromomaltose, the tetra-amylose being converted first into acetylated α-diamylose and the anhydride ring of this then opened by the further action of the acetyl bromide. The acetobromomaltose, which crystallises badly, may be identified by converting it, by means of silver carbonate, into hepta-acetylmaltose (E. and H. Fischer, A., 1910, i, 717) and further by hydrolysing the latter to maltose itself. Thus, α-diamylose is an anhydride of maltose, and since it does not reduce Fehling's solution, the acetal hydroxyl of the maltose (compare Haworth and Leitch, T., 1919, **115**, 809) must be united, with loss of water, with another hydroxyl of the sugar molecule, but whether this second hydroxyl is in the other or in the same glucose residue is unknown. α-Amylose is the first known anhydride of a disaccharide. T. H. P.

Polysaccharides. III. Cellulose. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1921, **4**, 174—184. Compare preceding abstract).—For any consideration of the structure of the cellulose molecule a knowledge of the maximum proportion of cellobiose obtainable from cellulose is of essential importance. The best method of isolating cellobiose from cellulose consists in hydrolysis by means of a mixture of acetic anhydride with a little concentrated sulphuric acid, and the highest yield of cellobiose octa-acetate yet obtained in this way is about 37%, this being formed at the ordinary temperature (Ost, A., 1913, i, 833); at higher temperatures the reaction proceeds more rapidly but gives poorer yields. In order to obtain information regarding the destruction of the cellose octa-acetate by the hydrolysing solution, the authors have treated cellulose, cellobiose, methylcelloside, cellulose triacetate, cellobiose acetate, and methylcelloside acetate with acetic anhydride and sulphuric acid under similar conditions, the resulting cellobiose octa-acetate being crystallised from alcohol and its amount determined. Comparison of the yields obtained in the different cases leads to the conclusion that cellulose must contain at least about 50%, and possibly more, of ready-formed cellobiose complex.

The formula for cellulose proposed by Hess and Wittelsbach (A., 1920, i, 532), improbable on other grounds, indicates only 33% of pre-formed cellobiose and cannot, therefore, be accurate; it is also incompatible with Pringsheim's observation (A., 1912, ii, 587) that cellobiose may be separated from cellulose without formation of dextrose. The formula for cellulose must be determined by that of cellobiose (compare Haworth and Leitch, T., 1919, **115**, 809; 1921, **119**, 193; Wrede, this vol., A., i, 161), and with the view of obtaining information concerning the constitution of cellobiose, the authors have methylated this sugar and subjected the methylcellobiose thus obtained to hydrolysis. Methylation of cellobiose

by means of alkali and methyl sulphate yields unsatisfactory results, since in faintly alkaline solution the methylation is incomplete, whilst in strongly alkaline solution partial hydrolysis and decomposition occur. If, however, the aldehyde group of the cellobiose is fixed by glucoside-formation, the methylation proceeds well. Methylation of methylcelloside by means of a large excess of methyl sulphate in concentrated (about 20%) sodium hydroxide solution gives an almost quantitative yield of hexamethylmethylcelloside. The latter may be further methylated, by means of dry methyl iodide and silver oxide, to heptamethyl-β(?)-methylcelloside, and hydrolysis of this by boiling with 5% hydrochloric acid solution yields a product from which β-tetramethylglucose may be isolated.

Hexamethyl methylcelloside, $C_{12}H_{15}O_4(OMe)_7$, crystallises in snow-white needles, m. p. 83—84°, $[\alpha]_D^{18}$ — 7·73° (in water), and *heptamethyl-β-methylcelloside*, $C_{12}H_{14}O_3(OMe)_8$, forms crystals, m. p. 86°, $[\alpha]_D^{20}$ — 15·91° (in water).

β-Tetramethylglucose has m. p. 94°, the value, 89°, given previously being low. T. H. P.

Polysaccharides. IV. Degradation of Potato Starch. P. KARRER and C. NÄGELI (*Helv. Chim. Acta*, 1921, **4**, 185—202. Compare A., 1920, i, 820).—The results of the experiments of Haworth and Leitch and of Haworth and Law (T., 1915, **107**, 8; 1916, **109**, 1314; 1918, **113**, 188, and 1919, **115**, 809) on the methylation of sucrose, lactose, melibiose, and maltose showed that glucosidic linkings are not destroyed by methylation with either methyl sulphate and alkali or methyl iodide and silver oxide. Methylation of methylcelloside in concentrated alkali hydroxide solution leads to a similar conclusion (Karrer and Widmer, preceding abstract).

The authors have completed and extended the experiments of Karrer (A., 1920, i, 820). Methylation by means of methyl iodide and silver oxide of potato starch purified by Malfitano and Moschkoff's method (A., 1910, i, 817) yields unsatisfactory results, but the use of methyl sulphate and baryta water leads to a methylostarch having the molecular weight (1) in water, 990—1026; on the assumption that the ash (1·1%) of the compound is admixed and not chemically combined, this value would be raised to about 1200 at the most; (2) in bromoform, 1689, this high result being probably due to association. Aqueous or chloroform solutions of the compound exhibit Tyndall's phenomenon and under the ultramicroscope show colloidal particles. The aqueous solutions, however, readily undergo ultrafiltration, leaving little on the filter, and the filtrates appear optically empty in the ultramicroscope and present no Tyndall effect; they are, therefore, true crystalloidal solutions, and they may be evaporated to dryness in a vacuum without alteration in the properties of the solute. Methylostarch is not attacked by either diastase or ptyalin, and *Bacillus macerans*, which degrades ordinary starch to crystalline dextrins, does not develop in its solutions or cause its depolymerisation. It is not transported by the electric current. This methylostarch,

$C_6H_8O_3(OMe)_2$, which contains about 32·6% of methoxyl, is converted by the action of methyl iodide and silver oxide into a product containing 35·5% of methoxyl and having the molecular weight about 1200 in water.

Methylation of potato starch by means of methyl sulphate and sodium hydroxide yields a product which contains about 35·5% of methoxyl, has the molecular weight 1830 in water, and forms an aqueous solution rendered optically empty by ultrafiltration.

As regards the magnitude of the starch molecule, the authors draw the conclusion that this molecule contains not more than six dextrose residues united by chemically normal linkings; the number of such residues may, indeed, be less than six, since it is not certain that the limits of depolymerisation are reached by the methylation. It may be that starch is a polymeric form of Schardinger's diamylose, that is, of maltose anhydride (this vol., i, 310), and similar to but more complex than tetra- and octa-amylose. Other non-saccharine polysaccharides also are probably polymerides of anhydro-sugars.

A reply is made to Hess's criticisms (this vol., i, 12). T. H. P.

Polysaccharides. V. Methylation of Inulin. P. KARRER and LINA LANG (*Helv. Chim. Acta*, 1921, **4**, 249—256).—The results obtained by the authors in some cases confirm, but in others contradict, those of Irvine and Steele (T., 1920, **117**, 1474).

Methylation of inulin by means of methyl sulphate and sodium hydroxide yields a product containing 39—39·7% of methoxyl, the proportions required for the di- and tri-methyl derivatives being 32·7% and 45·5% respectively. This product is soluble in alcohol, chloroform, acetone, or ether. Its aqueous solution, which is turbid and becomes more so when heated, becomes absolutely clear and optically empty when subjected to ultrafiltration, but is rendered turbid again when evaporated, even at 30°. The dry residue obtained on evaporation dissolves only incompletely in water. In phenol the product has the molecular weight 1650—1890, but in aqueous solution higher values are obtained, owing to imperfect dissolution.

The above methylated product is converted, when heated for a week with dry methyl iodide and silver oxide, into trimethylinulin, which, when dried in a vacuum at 90°, is obtained as a pulverulent solid, m. p. about 102—107°, $[\alpha]_D$ about $-43°$ (in chloroform), molecular weight in freezing phenol 1892. Irvine and Steele's description of trimethylinulin as an oil, $[\alpha]_D + 55·6°$ (in chloroform) is thus inaccurate. These authors state also that trimethylinulin may be partially distilled in a high vacuum, and they conclude that the molecule of inulin cannot be very large, but the present authors find that the distillate exhibits properties quite different from those of the original compound, so that it is not certain that the distillate contains unaltered trimethylinulin.

Irvine and Steele (*loc. cit.*, p. 1480) give a tetrasaccharide formula for inulin, but state later (p. 1481) that it is unlikely that inulin possesses a structure so simple as that of a tetrasaccharide. The

authors regard inulin as an associated or polymerised anhydro-sugar, which may be anhydrofructose, although this is not certain, no di- or tri-saccharide having been obtained by hydrolysis of inulin. That the fundamental basis of inulin is a saccharide composed of more than eight or ten fructose residues united by normal valencies is refuted by the author's molecular weight determinations.

T. H. P.

Polysaccharides. VI. Constitution of Starch and Glycogen. P. KARRER and C. NÄGELI (*Helv. Chim. Acta*, 1921, **4**, 263—269).—Although cellobiose, lactose, and even such sensitive disaccharides as sucrose and maltose are not decomposed at the ordinary temperature by acetyl bromide, the latter reacts with dry potato starch, yielding acetylbromomaltose in large proportions; the reaction follows the same course as that between diamylose or other α-amylose and acetyl bromide. The glucosidic linking being resistant towards acetyl bromide, the conclusion is drawn that, in starch, not more than two dextrose molecules are united by normal glucosidic valencies. In addition to the above way, starch may be hydrolysed by enzymes, by acid, and by *Bacillus macerans*, with formation of well-defined products, and a consideration of these indicates that starch is a polymerised maltose anhydride (diamylose); no higher polysaccharide than maltose is, indeed, obtained by the hydrolysis of starch.

The degree of polymerisation of starch is probably not very high, the high value formerly attributed to its molecular weight being presumed, wrongfully, from the insolubility. The polymerised α-amyloses exhibit the property, so characteristic for starch, of forming coloured additive compounds with iodine. So-called "soluble starches" and starch dextrins are to be regarded as polymerides of diamylose lower than starch, and they doubtless consist of mixtures of different polymerides difficult of crystallisation.

Glycogen is very closely allied to starch, yielding the same products as the latter when hydrolysed by either enzymes or acid. Glycogen must also be considered as a polymerised diamylose, the degree of polymerisation being different from that of starch. T. H. P.

Syntheses of Humins and Humic Acids. J. MARCUSSON (*Ber.*, 1921, **54**, [*B*], 542—545).—In their recent publication, Eller and Koch (A., 1920, i, 733) appear to have overlooked the fact that the author has recorded syntheses of humic acids from aldehydes of the furan series and from 5-hydroxymethylfurfuraldehyde (*Zeitsch. angew. Chem.*, 1919, **32**, 114) and also from furan-2-carboxylic acid (*Chem. Zeit.*, 1920, **44**, 44). The mechanism of the reaction in the latter case is difficult to explain, since the marked increase in the carbon content and diminution in the oxygen content cannot be entirely accounted for by the formation of anhydrides and ketones. Attention has therefore been directed to furan itself, which gives a pale brown, infusible resin when treated with concentrated hydrochloric acid which is converted by fusion with potassium hydroxide into a humic acid. Elementary analysis gives 65·5% C, 5·2% H, 0·7% Cl and 28·6% O. The

course of the reaction appears to be: furan → αδ-dihydroxydivinyl, $OH\cdot CH{:}CH\cdot CH{:}CH\cdot OH$, → succinaldehyde. Two molecules of the latter unite to form an aldol, which loses a molecule of water with formation of a *peri*difuran $\begin{array}{l}CH_2\cdot CH_2\!\!-\!\!-\!\!CH\cdot CHO\\ \Big| \qquad\qquad >O \quad \Big| \\ CH_2\cdot CH_2\!\!-\!\!-\!\!CH\cdot CHO\end{array}$. Similarly, fur furaldehyde is converted into succinaldehyde by the addition of two molecules of water and elimination of formic acid. The natural formation of humins occurs according to the scheme: cellulose → lævulose → (lævulic acid), hydroxymethylfurfuraldehyde, etc.

Eller and Koch's observation that humic acids are obtained from benzene derivatives is in harmony with the author's ideas, since the *peri*difuran ring may be regarded as a hexamethylene ring with an oxygen bridge. The complete identity of the synthetic and natural humic acids, however, cannot be regarded as completely established, since the latter, unlike benzene derivatives, cannot be sulphonated or nitrated.

The acidity of the humic acids has been ascribed by Eller and Koch to the presence of phenolic hydroxyl groups; the ready, if incomplete, esterification of these substances when heated with alcoholic hydrogen chloride (3%) and the elimination of carbon dioxide when they are heated at 250° in the presence of steam seems, however, to indicate the presence of carboxyl groups.

H. W.

Preparation of Amines of Secondary Alcohols. ALPHONSE MAILHE (*Compt. rend.*, 1921, **172**, 692—694; *Bull. Soc. chim.*, 1921, [iv], **29**, 219).—The method of hydrogenation of ketazines of symmetrical ketones (compare A., 1920, i, 475) has been extended to the ketazines of unsymmetrical ketones.

Methyl *iso*propyl ketone yields *bis-methyl*iso*propylketazine*, $CHMe_2\cdot CMe{:}N\cdot N{:}CMe\cdot CHMe_2$, b. p. 165°, which on hydrogenation gives *γ-amino-β-methylbutane*, b. p. 76—78°, forming a *phenylcarbamide*, m. p. 144°, and *bis-αβ-dimethylpropylamine*, $NH(CHMe\cdot CHMe_2)_2$, b. p. 178—180°. Similarly, methyl propyl ketone gives a *ketazine*, b. p. 198—200° which yields *β-aminopentane*, $NH_2\cdot CHMe\cdot CH_2Et$, b. p. 86—88°, with a *phenylcarbamide*, m. p. 115°, and *bis-α-methylbutylamine*, $NH(CHMePr)_2$, b. p. 185—188°. *Bis-methyl*iso*butylketazine*, b. p. 176° yields *α-methyl*iso*amylamine*, $NH_2\cdot CHMe\cdot CH_2\cdot CHMe_2$, b. p. 108—110°, giving a *phenylcarbamide*, m. p. 108°, and *bis-αγ-dimethylbutylamine*, $NH(CHMe\cdot CH_2\cdot CHMe_2)_2$, b. p. 208—210°. *Bis-methyl*iso*amylketazine*, b. p. 155—160°/45 mm., yields *ε-amino-β-methylhexane*, $CHMe_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$, b. p. 137°, giving a *phenylcarbamide*, m. p. 103°, and *bis-αδ-dimethylamylamine*,

$$NH(CHMe\cdot CH_2\cdot CH_2\cdot CHMe_2)_2,$$

b. p. 240°. *Bis-*iso*propyl*iso*butylketazine*, b. p. 190—195°, yields *δ-amino-βε-dimethylhexane*, $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CHMe_2$, b. p. 145—148°, and *bis-γ-methyl-α-*iso*propylbutylamine*,

$$NH[CH(CHMe_2)\cdot CH_2\cdot CHMe_2]_2,$$

b. p. 245°.

W. G.

Influence of Double Linkings on the Co-ordination Number. A. PIERONI (*Gazzetta*, 1921, **51**, i, 42—47. Compare A., 1914, i, 1200).—Treatment of cobalt and chromium salts under suitable conditions with allylamine yields various products, but the only one to which a formula can be ascribed in accord with its properties has the composition, $Co(C_3H_5{\cdot}NH_2)_6O_6Cl_3$. This compound, which is obtained by suspending the additive compound, $CoCl_2,3C_3H_5{\cdot}NH_2$, in an anhydrous alcoholic solution of allylamine and passing through the liquid a slow current of oxygen, yields a neutral aqueous solution becoming strongly alkaline when boiled and giving, only slowly and after some time, a precipitate of cobalt hydroxide when treated with potassium hydroxide in the cold; distillation of the compound with potassium hydroxide results in the complete liberation of the unaltered allylamine. Further, the product exhibits oxidising properties, as it sets free iodine from potassium iodide, and also rapidly reduces permanganate solution. Compounds possessing somewhat analogous peroxidic properties exist in Werner's series and are represented by the general formulæ, $Co_2O_2(NH_3)_{10}X_4 + mH_2O$ and $Co_2O_2(NH_3)_{10}Cl_5$. The complex cobalt compound obtained consumes more permanganate than is required by the unsaturated base it contains, but the excess corresponds with only one of the six oxygen atoms present. It may, therefore, be assumed that this oxygen atom alone can be liberated in the atomic condition from the complex, to which the formula, $\left[Co\,{}^{(C_3H_5{\cdot}NH_2)_6}_{2O_2}\right]Cl_3H_2O_2$, may be attributed; the presence of hydrogen peroxide may be detected by means of titanium sulphate. Thus the complex has the co-ordination number eight, whereas, according to Werner's theory, this number should be six. It is suggested that additive products and complex salts are formed as a result of differences of chemical potential existing, under certain experimental conditions, between the reacting components, and the conclusion is drawn that the co-ordination number is not fixed but increases as such potential difference increases and as the influence of the solvent diminishes.

The *additive compound*, $CoCl_2,3C_3H_5{\cdot}NH_2$, forms red needles, is decomposed immediately by water, producing an alkaline reaction, and absorbs atmospheric moisture with avidity, forming a pitch-like mass.

The *complex*, $\left[Co\,{}^{(C_3H_5{\cdot}NH_2)_6}_{2O_2}\right]Cl_3H_2O_2$, forms a violet-red powder or minute, acicular crystals, decomposing without melting at 120—140°. T. H. P.

Complex Metallic Ammines. V. *cis*-Succinatodiethylenediaminecobaltic Salts, and other Cobaltammine Salts containing a Seven-membered Ring in the Complex. JAMES COOPER DUFF (T., 1921, **119**, 385—390).

Compounds of Hexamethylenetetramine with Complex Metallic Salts and Acids. PRIYADARANJAN RÂY and PULIN VIHARI SARKAR (T., 1921, **119**, 390—396).

Action of Hydrogen Peroxide on Hexamethylenetetramine. C. VON GIRSEWALD and HANS SIEGENS (*Ber.*, 1921, **54**, [*B*], 490—491).—Repetition of Leulier's work (A., 1917, i, 252) has shown that the peroxide, $NH(CH_2{\cdot}CH_2{\cdot}O{\cdot}OH)_2$, described by him is in reality hexamethylenetriperoxidediamine, $N(CH_2{\cdot}O{\cdot}O{\cdot}CH_2)_3N$ (compare Baeyer and Villiger, A., 1900, i, 626; von Girsewald, A., 1912, i, 834); the error is due to a mistake in the estimation of nitrogen.

H. W.

Preparation of Alkyliminodisulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 330801; from *Chem. Zentr.*, 1921, ii, 600—601).—The basic salts of iminodisulphonic acid are treated with organic halogen compounds or esters of inorganic acids and the salts of the alkyliminodisulphonic acids thus produced are decomposed. Reaction between organic halogen compounds, such as methyl iodide, epichlorohydrin, and ethylene bromide, or esters, such as methyl sulphate, and potassium or sodium iminodisulphonates occurs in accordance with the scheme: $KN(SO_3K)_2 + RCl = KCl + R{\cdot}N(SO_3K)_2$. The alkyliminodisulphonates lose one sulphonic group when gently treated with acids and both sulphonic groups under more drastic conditions, giving alkyliminomonosulphonic acids and alkylamines respectively. Potassium methyliminodisulphonate, prepared from methyl iodide or sulphate and an aqueous solution of potassium iminodisulphonate in the presence of potassium hydroxide, is unchanged in aqueous solution, but loses one sulphonic group when warmed with hydrochloric acid, and is decomposed completely by protracted boiling with the same acid. *Potassium dihydroxypropyliminodisulphonate*, $N(SO_3K)_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, is obtained by the use of epichlorohydrin at the ordinary temperature; it is stable in alkaline or neutral solution, but decomposed by boiling acids into sulphuric acid and dihydroxypropylamine. *Potassium ethylenediaminetetrasulphonate* is prepared by boiling an aqueous solution of potassium iminodisulphonate and potassium hydroxide with ethylene bromide; it gives ethylene diamine under the influence of acids. If an aqueous suspension of potassium methyliminodisulphonate is heated to boiling for a short period with a little sulphuric acid and the latter is subsequently removed by barium hydroxide and carbon dioxide, potassium methylaminomonosulphonate is obtained in shining leaflets; protracted boiling with mineral acids is necessary for the decomposition of the latter into sulphuric acid and methylamine.

H. W.

The Amphoteric Properties of some Amino-acids and Peptides. HERBERT ECKWEILER, HELEN MILLER NOYES, and K. GEORGE FALK (*J. Gen. Physiol.*, 1921, **3**, 291—308).—Titration curves are worked out for glycine, alanine, α-aminobutyric acid, leucine, glycylglycine, alanylglycine, and alanylalanine; also for sodium chloride, carbamide, acetone, acetamide, acetic acid, and aceturic acid.

Carbamide, acetamide, acetone, and water give identical curves;

acetic acid and aceturic acid are identical with water on the acid side, but on the alkaline side both show a buffer action, that of aceturic acid being more pronounced.

The four amino-acids give identical curves, as do also the dipeptides; the latter, however, show a much stronger buffer action, owing, apparently, to the presence of the –CO·NH– group. The isoelectric points of some of the amino-acids and dipeptides were determined.

The definition, significance, and theoretical deduction of the isoelectric point are discussed at some length. C. R. H.

Butyl- and *iso*Butyl-cyanoacetic Acids. JOHN C. HESSLER and WILLIAM F. HENDERSON (*J. Amer. Chem. Soc.*, 1921, **43**, 672—676).—*iso*Butylation of ethyl cyanoacetate in *iso*butyl alcoholic solution gives *iso*butyl esters. From *iso*butylcyanoacetic acid the *zinc*, *calcium*, *lead*, and *cadmium* salts were prepared. Di*iso*butylcyanoacetic acid (Freylon, A., 1910, i, 358) was characterised by its iso*butyl ester*, $CN·C(C_4H_9)_2·CO_2·C_4H_9$, b. p. 155—160°/25 mm., 250—260°/739 mm., D^{19} 0·9118; the *barium*, *calcium*, *cadmium*, and *cobalt* salts were obtained. Butylcyanoacetic acid (Hadley, A., 1912, i, 699) was characterised by its *butyl* ester, $C_{11}H_{19}O_2N$, b. p. 157—161°/30 mm., 255—260°/739 mm., D^{21} 0·9369; the *silver* and *cadmium* salts were prepared. Dibutylcyanoacetamide forms needles, m. p. 123°. J. K.

Further Experiments on the Bromination of Unsaturated Compounds with *N*-Bromoacetamide. A. WOHL and K. JASCHINOWSKI (*Ber.*, 1921, **54**, [*B*], 476—484).—Further confirmation is obtained of the rule propounded previously (A., 1919, i, 198) that bromination is only effected by this reagent with substances which are unsaturated and contain a reactive hydrogen atom.

In contrast with βγ-dimethyl-Δ^{β}-butylene, ββγγ-tetramethylbutane is not attacked by bromoacetamide. The inactivity of cinnamic acid, its ester or aldehyde and of fumaric or maleic acid which is caused by the presence of the negative phenyl or carbonyl group disappears when an ethoxy- or methyl-group is suitably introduced. Thus crotonic acid gives a *monobromocrotonic acid*, m. p. 83°, b. p. 105—107°/1·3 mm., ethyl β-ethoxycinnamate yields *ethyl α-bromo-β-ethoxycinnamate*, OEt·CPh:CBr·CO_2Et, pale yellow liquid, b. p. 120—125°/0·12 mm. (the position of the bromine atom is established by its conversion by ozone into oxalic and benzoic acids), whilst ethyl β-ethoxycrotonate gives *ethyl γ-bromo-β-ethoxycrotonate*, $CH_2Br·C(OEt):CH·CO_2Et$, b. p. 83°/0·1 mm. In general, the compounds obtained are less symmetrical than the original unsaturated substances, and their isolation is rendered difficult by the extensive formation of resinous polymerides. In contrast to acetylene and ethylene (*loc. cit.*), propylene is slowly converted into a dibromide, probably $CH_2Br·CBr:CH_2$, b. p. 140·5—141·5°. The additive capacity of α-phenylpropinene, CPh:CMe, is restricted by the presence of the phenyl group, but an unsaturated dibromo-*compound*, $C_9H_6Br_2$, is slowly formed which was not

obtained free from the parent substance and in which the position of the halogen atoms could not be fully elucidated by reason of the small amount of available substance. An active hydrogen atom is not present in styrene and the action of bromoacetamide on the latter therefore yields only the saturated styrene dibromide, $CHPhBr\cdot CH_2Br$. Allyl alcohol, on the other hand, readily gives a mixture of mono- and di-bromoallyl alcohols, b. p. 102—104°/11 mm.; allyl ether, even at a low temperature, reacts with evolution of bromine. The presence of bromine inhibits addition in the case of allyl bromide to a considerable extent, but a mixture of di- and tri-bromopropylene is slowly formed. Formic acid, and methyl and ethyl formates are violently attacked by bromoacetamide with evolution of large amounts of gas; the observation in the case of the acid is of considerable interest, since it has been shown to be completely stable towards free bromine.

The action of *N*-bromophthalimide towards ethyl acetoacetate is similar to that of bromoacetamide, and leads to the formation of ethyl α-bromoacetoacetate. On the other hand, chloro- and bromo-imidocarbonic esters do not react with ethylacetoacetate.

H. W.

_d_-Ribohexosamic Acids. P. A. LEVENE and E. P. CLARK (*J. Biol. Chem.*, 1921, **46**, 19—33).—A method is described in detail, by which 1·5 kilos. of ribose were prepared from yeast-nucleic acid by way of the pure nucleosides. From amino-*d*-riboside (A., 1915, i, 601) two new epimeric d-*ribohexosamic acids*, $C_6H_{13}O_5N$, have been obtained (by addition of hydrogen cyanide), thus completing the series of eight *d*-hexosamic acids (compare A., 1917, i, 631; 1918, i, 530, 532). The optical rotations of these are discussed, and it is considered likely that chitosamic (glucosamic) acid has the configuration of mannonic, epichitosamic of gluconic, dextro-xylohexosamic of gulonic, *l*-xylohexosamic of idonic, chondrosamic of talonic, epichondrosamic of galactonic, *d*-ribohexosamic of allonic, and lævo-ribohexosamic of altronic acid.

Of the two *d*-ribohexosamic acids now prepared, the *lævorotatory* is the less soluble, and obtained more readily by crystallisation of the synthetic mixture; it has m. p. 212°, $[\alpha]_D^{20}$—26·0°; its *lactone hydrochloride*, $C_6H_{12}O_5NCl$, has m. p. 188°, $[\alpha]_D^{20}$—11·0°. The epimeric *dextrorotatory acid* has m. p. 186°, $[\alpha]_D^{20}$ + 12·5°; its *lactone hydrochloride* has m. p. 150°, $[\alpha]_D^{20}$ + 21·5°. *Dibenzylidene-dextro*-d-*ribohexosamic ethyl ester*, $C_{22}H_{26}O_6NCl$, m. p. 221°, $[\alpha]_D^{20}$ − 26° (in methyl alcohol). After de-amination, lævo-*d*-ribohexosamic acid is oxidised by nitric acid to αα-anhydro-allomucic acid, the dextrorotatory acid to αα-anhydrotalomucic acid. Both these acids give calcium salts, $C_6H_6O_7Ca,3H_2O$; that of the former acid is optically inactive and becomes anhydrous at 130° under reduced pressure; the salt of αα-anhydrotalomucic acid has $[\alpha]_D^{20}$ — 9° and retains one H_2O under the same conditions. G. B.

Some Amides of Acids of the Sugar Group. Relation between Constitution and Rotatory Power. W. E. VAN WIJK (*Rec. trav. chim.*, 1921, **40**, 221—246).—An extension of Marle's

study (A., 1920, i, 592) of Hudson's rule (A., 1917, i, 318) in its applicability to the rotatory power and configuration of derivatives of acids of the sugar group. The following derivatives have been prepared.

l-Arabonic acid gives a *methylamide*, m. p. 170°; $[\alpha]_D^{12}$ + 51·1° (in water); a *benzylamide*, m. p. 167°; $[\alpha]_D^{10}$ + 45·8° (in water); a β-*phenylethylamide*, m. p. 173·5°; $[\alpha]_D^{12}$ + 24° (in water); a β-p-*hydroxyphenylethylamide*, m. p. 164°; $[\alpha]_D^{15}$ + 23·5° (in water); a β-*naphthylamide*, m. p. 214°; a *tetramethylenediamide*, m. p. 194°; $[\alpha]_D^{13}$ + 36·3° (in water); *methyl* l-*arabonylaminoacetate*, m. p. 104°; $[\alpha]_D^{16}$ + 44·8° (in water); and *ethyl* l-*arabonylaminoacetate*, m. p. 124°; $[\alpha]_D^{10}$ + 43·3° (in water).

d-Galactonic acid gives a *methylamide*, m. p. 153°; $[\alpha]_D^{10}$ + 34·5° (in water); a *benzylamide*, m. p. 187°; $[\alpha]_D^{17}$ + 55·2° (in water); a β-*phenylethylamide*, m. p. 198°; $[\alpha]_D^{14}$ + 21·9° (in water); a β-*naphthylamide*, m. p. 214°.

d-Mannonic acid gives an amide, m. p. 176°; $[\alpha]_D^{12}$ − 17·2° (in water) (compare Hudson and Komatsu, A., 1919, i, 524); a *methylamide*, m. p. 165—166°; $[\alpha]_D^{12}$ − 18·1° (in water); an anilide, m. p. 176°; $[\alpha]_D^{12}$ − 16·9° (in water); a m-*toluidide*, m. p. 142°; a p-*toluidide*, m. p. 179°; $[\alpha]_D^{10}$ − 18·1° (in water); a *benzylamide*, m. p. 164°; $[\alpha]_D^{12}$ − 9·1° (in water); a β-*phenylethylamide*, m. p. 166°; $[\alpha]_D^{11}$ − 7·5° (in water).

d-Gluconic acid gives a *methylamide*, m. p. 127° (decomp.); $[\alpha]_D^{12}$ + 33·8° (in water); a m-*toluidide*, m. p. 158°; $[\alpha]_D^{12}$ + 48·7° (in water); a *benzylamide*, m. p. 163°; $[\alpha]_D^{12}$ + 16·1° (in water); a β-*phenylethylamide*, m. p. 151°; $[\alpha]_D^{12}$ + 11·1°; and α-*naphthylamide*, m. p. 178°; $[\alpha]_D^{20}$ + 37·9° (in water); and a β-*naphthylamide*, m. p. 190°.

The results indicate that Hudson's law (*loc. cit.*) holds equally for the methylamides, benzylamides, and phenylethylamides in aqueous solution. Tschugaev's rule (A., 1898, ii, 495) that the influence exercised by an inactive substituent on the rotation diminishes as its distance from the asymmetric complex increases, is confirmed by some of the anilides, benzylamides, and β-phenylethylamides. The introduction of a phenyl radicle into the amide group has a greater effect on the rotation than the introduction of a methyl radicle. Comparing the rotatory powers of the *o*-, *m*-, and *p*-toluidides with those of the anilides gives confirmation of the relation given by Frankland and Wharton (T., 1896, **69**, 1320), para > meta > phenyl > ortho. Only with great difficulty can *o*-toluidine be caused to react with the lactones of the acids of the sugar group; and only in one case did α-naphthylamine condense with a lactone, namely, that of *d*-gluconic acid. W. G.

Preparation of Carbamide from Compounds of Ammonia and Carbon Dioxide. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 332679; from *Chem. Zentr.*, 1921, ii, 647).—In the apparatus employed, a pressure of 15 atmospheres can be maintained during all the operations. Ammonium carbamate, formed by the union of carbon dioxide and ammonia at 90°, with a little water (for

example, in the ratio 10 : 1) is passed slowly through a pressure-tight spiral tube maintained at 135—140°. The mixture leaving after two to three hours has 25% or more of its original ammonium carbamate changed into carbamide. G. W. R.

Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. I. The Amides and s.-Di-alkyl- and -aryl-substituted Amides of Mono- and Di-bromomalonic Acid. JOHN VALENTINE BACKES, RALPH WINTON WEST, and MARTHA ANNIE WHITELEY (T., 1921, **119**, 359—379).

Cause and Composition of the Insoluble Deposits in Oil of Mustard. HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1921, **259**, 16—33).—Natural and synthetic oil of mustard becomes discoloured when preserved and slowly deposits a dark orange to citron-yellow precipitate. The latter consists of a cauliflower-like coloured mass in which are contained colourless quadratic prisms and small quantities of hexagonal plates, cubes, and slender, prismatic needles. A portion of the deposit is soluble in water, and this consists principally of allylamine sulphate possibly admixed with traces of ammonium sulphate. The chief constituent of the portion insoluble in water is ψ-thiocyanogen, $C_3HN_3S_3$, whilst *iso*perthiocyanic acid, $\begin{matrix}CS\cdot NH \\ NH-CS\end{matrix}\!\!>\!S$, and allyl-substituted carbamides are most probably also present.

The following mechanism of the process appears most likely. Oil of mustard generally contains varying amounts of carbon disulphide and allyl cyanide, and its changes in colour and composition are to be regarded as consecutive reactions. The first phase consists in the decomposition of the allylthiocarbimide into allyl cyanide and free sulphur, whilst further molecules become dissociated into the $S\colon C\colon$ and $\colon N\cdot C_3H_5$ groups. A portion of the sulphur dissolves in unchanged allylthiocarbimide, and causes the initial yellow coloration of the oil, a second portion combines with the $\colon C\colon S$ group to form CS_2, whilst a third portion becomes oxidised to sulphuric acid. The latter combines with allylamine, formed from the $\colon N\cdot C_3H_5$ groups. The two reactions last mentioned are due to the conjoint action of atmospheric oxygen and moisture, which is catalytically accelerated in the presence of light by unchanged oil, which itself becomes partly polymerised during the process. The group, $\colon C\colon S$, appears also to be fundamental in the formation of xanthic acid derivatives, $S\colon C\colon + S\colon C\colon N\cdot C_3H_5 + H_2O \longrightarrow HS\cdot CS\cdot O\cdot C_3H_5 + HCN$, and the hydrocyanic acid which is thus liberated becomes polymerised and reacts with sulphur to form ψ-thiocyanogen, $3HCN + 3S = C_3HN_3S_3 + H_2$; the hydrogen which is thereby set free converts the group $\colon N\cdot C_3H_5$ into allylamine. H. W.

Preparation of Guanidine Salts. FRANZ HOFWIMMER (D.R.P. 332681; from *Chem. Zentr.*, 1921, ii, 647—648).—Cyanamides of the alkaline earth metals are heated with ammonium salts at suitable temperatures. For example, calcium cyanamide heated with

ammonium nitrate at 200—220° gives guanidine nitrate, $CaCN_2 + 3NH_4 \cdot NO_3 = NH{:}C(NH_2)_2,HNO_3 + Ca(NO_3)_2 + 2NH_3$. The guanidine salt can be separated by crystallisation and ammonium nitrate can be regenerated, using the calcium nitrate and ammonia formed in the reaction. G. W. R.

Synthesis of Cyanic Acid and Carbamide by Oxidation in Ammoniacal Solution of Alcohols, Phenols, and Aldehydes. R. Fosse and G. Laude (*Compt. rend.*, 1921, **172**, 684—686. Compare this vol., i, 165).—By oxidation in ammoniacal solution with potassium permanganate alone or in the presence of ammonium sulphate, copper carbonate, or copper powder, methyl, ethyl, and butyl alcohols, phenol, *o*-cresol, α- and β-naphthols, catechol and resorcinol, acetaldehyde, propaldehyde, and butaldehyde all give cyanic acid, which is converted into carbamide by the action of ammonium chloride. W. G.

Synthesis of Cyanic Acid by Oxidation of Organic Substances. New Methods of Detecting the Substance. R. Fosse (*Bull. Soc. Chim.*, 1921, [iv], **29**, 158—203).—A résumé of work already published (A., 1912, i, 519, 541, 668, ii, 1203; 1913, i, 327, 432, 947, 1020; 1914, ii, 154, 506, 593, 756; 1917, i, 73; 1919, i, 152, 297, 313, 459; 1920, ii, 714, 779). W. G.

Condensation of Methylene Dicyanide with Ketones and Aldehydes. G. J. Östling (*Ofversicht Finska Vetenskaps Soc. Forhändl.*, 1915, **57**, [*A*], No. 11, 13 pp.; from *Chem. Zentr.*, 1921, i, 613).—An investigation of the condensations of methylene dicyanide with ketones and aldehydes. Methylene dicyanide and acetone in molecular proportions give, in presence of a little piperidene, a colourless, crystalline *substance*, $C_{15}H_{14}N_6$, volatile at 400°, easily soluble in sodium hydroxide and potassium hydroxide. Condensation of methylene dicyanide with a large excess of acetone (in alcoholic, ethereal, or aqueous solution) gives clear crystals which, when heated with concentrated hydrochloric acid in a bomb tube at 150° for five to six hours give an *acid*, $C_{17}H_{24}O_4N$, yellow needles, m. p. 152—153°. From the portion of the condensation products melting at lower temperatures, a crystalline *acid* could be extracted by potassium hydroxide. Other condensation products were obtained with methyl ethyl ketone, acetylacetone, and diethyl ketone. Condensation with benzaldehyde in alcohol gives a compound, $CHPh{:}C(CN)_2$, m. p. 88°. With formaldehyde in water, plates, m. p. 206—207°, of a probable *polymeride* of the formula $CH_2{:}C(CN)_2$ were obtained. With acetaldehyde needles of a *substance*, $CHMe{:}C(CN)_2$, m. p. 77—78° (from alcohol) were obtained. G. W. R.

Action of Sulphuric Acid on Dicyanodiamide. Tenney L. Davis (*J. Amer. Chem. Soc.*, 1921, **43**, 669—672).—The formation of guanidine by the action of 61% sulphuric acid on dicyanodiamide (Lidholm, A., 1913, i, 252, 451) is slow at 100°, but an 85% yield is obtained after six hours at 140°, and only slightly improved at 200°. At the higher temperature, carbon dioxide is produced in

excess of that calculated, probably owing to some hydrolysis of the guanidine. J. K.

Copper–Cyanogen Compounds. E. MOLES and R. IZAGUIRRE (*Anal. Fís. Quím.*, 1921, **19**, 33—93).—The authors have investigated the reactions between potassium cyanide and various salts of copper in aqueous solution by physico-chemical means. Measurements of conductivity, density, and other physical properties were made and plotted against the ratio Cu : CN in every case. Separate series of curves were made for 0°, 18°, and 25° respectively. The existence of definite compounds is deduced from the occurrence of discontinuities on the curves obtained.

At 0°, the curves show the formation of three compounds, namely, $K_2Cu(CN)_4$, soluble and colourless, $K_2Cu[Cu(CN)_4]_2$, soluble, violet and $CuCu(CN)_4$, insoluble, yellow. The curves at higher temperatures have a different form, indicating the extreme instability of these compounds, which, even when prepared at 0°, decompose when kept, forming cuprous cyanide.

The formula suggested for the yellow precipitate was confirmed by analysis and conductivity measurements on the first of the compounds mentioned above, prepared from it by reaction with the required amount of potassium cyanide in aqueous solution.

The measurement of conductivity, working at 0°, is suggested as a basis for the rapid volumetric estimation of copper, since a well-defined maximum occurs on the resistance curve at the ratio Cu : 2CN. G. W. R.

Thallous Ferricyanide. V. CUTTICA and G. CANNERI (*Gazzetta*, 1921, **51**, i, 169—174).—Thallous ferrocyanide separates as a yellow, anhydrous, microcrystalline powder of the formula $Tl_4Fe(CN)_6$ when a concentrated solution of a thallous salt is treated with a deficit of potassium ferrocyanide, and appears to exist in two isomeric forms (compare Briggs, T., 1911, **99**, 1020). Fischer and Benzian's so-called double salt, $K_4Fe(CN)_6,K_3TlFe(CN)_6,6H_2O$ (A., 1902, i, 272), appears to be one of a series of solid solutions of thallous ferrocyanide in potassium ferrocyanide.

Thallous ferricyanide, $Tl_3Fe(CN)_6$, prepared by treating either lead or silver ferricyanide with a thallous salt or by oxidation of the ferrocyanide, forms intense reddish-brown, microscopic prisms, and, like the lead salt, is readily soluble in water. When treated in solution with hydroxides of the alkali or alkaline-earth metals, it is decomposed with deposition of thallium sesquioxide, whilst hot mineral acids decompose the salt with liberation of hydrocyanic acid. When heated at about 150° the salt does not decompose, but it then gives a green, aqueous solution turned yellow by addition of alkali; a similar phenomenon occurs with potassium ferricyanide and may be due to isomeric change.

In the estimation of thallium as chromate (Browning and Hutchins, A., 1900, ii, 172; Rupp and Zimmer, A., 1903, ii, 183), the following procedure is recommended. The thallous chromate, collected under pressure on a filter supported by a platinum cone, is washed with 80% alcohol, in which it is practically insoluble,

until the filtrate shows no reaction for chromic acid. It is then dissolved in dilute sulphuric acid and estimated iodometrically with thiosulphate, addition of potassium iodide causing separation of thallous iodide and of iodine: 3I correspond with Tl_2O. The solution to be titrated should contain a quantity of thallium corresponding with about 0·2 gram of thallous chromate, 100 c.c. of 2*N*-sulphuric acid being taken and the liquid diluted to 400 c.c. After addition of 2 grams of potassium iodide, the solution is titrated with *N*/10-thiosulphate in presence of starch paste; the end-point is shown by the colour changing from dark green to golden-yellow. This method is more rapid, but gives results somewhat lower, than the gravimetric method. T. H. P.

Aliphatic Diazo-compounds. XX. Reduction by Means of Hydrogen in Presence of Palladium. H. STAUDINGER, ALICE GAULE, and J. SIEGWART (*Helv. Chim. Acta*, 1921, **4**, 212—217. Compare this vol., i, 245).—It has been shown previously (A., 1916, i, 853) that hydrazi-compounds very readily undergo rearrangement into hydrazones, and it seemed possible, assuming Curtius's formulation for diazo-compounds, that the latter should yield on reduction highly unstable hydrazi-derivatives and that these would then pass into hydrazones. The reduction of aliphatic diazo-compounds by means of hydrogen in presence of colloidal platinum, that is, in neutral solution, has now been investigated, the results obtained being in accord with the Angeli-Thiele formulation for diazo-compounds.

With diphenyldiazomethane the principal product is diphenylmethane, benzophenone hydrazone being formed in smaller proportion. The reaction is probably expressed by the scheme: $CPh_2{:}N{\cdot}NH_2 \longleftarrow CPh_2{:}N{:}N \longrightarrow CHPh_2{\cdot}N{:}NH \longrightarrow CH_2Ph_2 + N_2$, and is similar to the formation of hydrocarbons by reduction of aromatic diazo-compounds by means of an alkaline solution of a stannous salt. Analogous behaviour is exhibited by diphenylenediazomethane, which is reduced almost quantitatively to fluorene, and by ethyl diazoacetate which, to the extent of 60—70%, is converted into ethyl acetate, and also yields a crystalline *compound*, $C_{12}H_{22}O_6N_2$, m. p. 97—98°. Ethyl diazomalonate yields ethyl oxomalonatehydrazone, $N{:}N{:}C(CO_2Et)_2 \longrightarrow NH_2{\cdot}N{:}C(CO_2Et)_2$ (Neeresheimer, Diss., Munich, 1908).

With most diazo-compounds, reduction by means of aluminium amalgam in ethereal solution, that is, in perfectly neutral solution, follows a different course. Thus, diphenyldiazomethane is readily reduced, with liberation of ammonia, to diphenylmethylamine, the intermediate formation of benzophenonehydrazone being probable: $N{:}N{:}CPh_2 \rightarrow NH_2{\cdot}N{:}CPh_2 \rightarrow NH_2{\cdot}NH{\cdot}CHPh_2 \rightarrow NH_2{\cdot}CHPh_2 + NH_3$. Diphenylenediazomethane yields ammonia and fluorene under these conditions, and since fluorenonehydrazone is also reduced to fluorene by aluminium, diphenylenemethylamine must be highly unstable. With ethyl diazoacetate, ammonia is liberated and an aluminium compound of glycine ester, but no ethyl acetate, formed.

T. H. P.

Aliphatic Diazo-compounds. XXI. Constitution of the Hydrazones, especially of Ethyl Mesoxalatehydrazone. H. STAUDINGER and L. HAMMET (*Helv. Chim. Acta*, 1921, **4**, 217—228).—Reduction of ethyl diazomalonate by Paal's method (preceding abstract) yields a hydrazine derivative which was at first regarded as ethyl hydrazimalonate :

$$C(OH)_2(CO_2Et)_2 \longrightarrow NH_2{\cdot}NH{\cdot}C(CO_2Et)_2{\cdot}OH$$

(isolated by Curtiss, Koch, and Bartells, A., 1909, i, 212),

$$\longrightarrow \begin{matrix}NH\\|\\NH\end{matrix}\!\!>C(CO_2Et)_2.$$

This assumption was supported by the fact that Curtiss's ethyl phenyliminomalonate, unlike the hydrazone, is coloured and, like ethyl oxomalonate, a highly reactive compound. Further, unlike the true hydrazones, the product of the above reaction, when treated with benzaldehyde, does not form a mixed azine, but reacts only after prolonged heating, with formation of benzaldazine; moreover, it reacts slowly with phenylcarbimide and not at all with diphenylketen, whereas true hydrazones react vigorously with these reagents.

The product is, nevertheless, a true hydrazone, having the formula $NH_2{\cdot}N{:}C(CO_2Et)_2$. In benzene solution it forms double molecules, the proportion of which increases with the concentration of the solution. This behaviour is incompatible with the hydrazimalonate ring formula, but is readily explainable by the open-chain hydrazone formula, since many ethyl oxomalonate derivatives have a very unstable double linking and pass readily into ethyl mesoxalate derivatives. Thus, the solid hydrazone probably represents such an ethyl mesoxalate derivative,

$$NH_2{\cdot}NH{\cdot}C(CO_2Et)_2{\cdot}NH{\cdot}N{:}C(CO_2Et)_2$$

or $C(CO_2Et)_2{<}\begin{matrix}NH{\cdot}NH\\NH{\cdot}NH\end{matrix}{>}C(CO_2Et)_2$, whilst the dilute benzene solution contains principally the ethyl oxomalonate.

The hydrazone formula is supported also by the behaviour of *as.*- and *s.*-dimethylhydrazine with ethyl mesoxalate. The former yields ethyl oxomalonatedimethylhydrazone, which, since the formation of double molecules is here excluded, exhibits the normal molecular weight :

$$C(OH)_2(CO_2Et)_2 \rightarrow OH{\cdot}C(CO_2Et)_2{\cdot}NH{\cdot}NMe_2 \rightarrow C(CO_2Et)_2{:}N{\cdot}NMe_2.$$

s.-Dimethylhydrazine should yield ethyl dimethylhydrazimalonate, on the assumption that the hydrazimalonic ester is formed with hydrazine :

$$C(OH)_2(CO_2Et)_2 \rightarrow OH{\cdot}C(CO_2Et)_2{\cdot}NMe{\cdot}NHMe \rightarrow C(CO_2Et)_2{<}\begin{matrix}NMe\\|\\NMe\end{matrix}.$$

With ethyl mesoxalate, *s.*-dimethylhydrazine reacts with great difficulty, whereas with ethyl oxomalonate it reacts readily, but does not yield the product expected. In addition to hydrazine and its *as.*-dimethyl-compound, the aromatic hydrazine derivatives also yield normal hydrazones with ethyl oxomalonate or mesoxalate; similar behaviour is shown by hydroxylamine, which yields ethyl oximinomalonate. On the other hand, with phenyl-

semicarbazide and with benzoylhydrazine, stable hydrates, that is, ethyl mesoxalate derivatives, are obtained, these being converted into ethyl oxomalonate derivatives by treatment with phosphorus pentoxide; the action of aniline on oxomalonic ester proceeds similarly:

$$C(OH)_2(CO_2Et)_2 \longrightarrow OH\cdot C(CO_2Et)_2\cdot NH\cdot NH\cdot CO\cdot NHPh \longrightarrow C(CO_2Et)_2\colon N\cdot NH\cdot CO\cdot NHPh.$$

The $\colon N\cdot NH_2$ group of different hydrazones behaves differently towards benzaldehyde (Staudinger and Kupfer, A., 1911, i, 751). The authors find that the behaviour towards phenylcarbimide and diphenylketen of hydrazones of carbonyl compounds varies widely with the nature of the original aldehyde or ketone. The phenylsemicarbazones prepared from phenylcarbimide and hydrazones are identical with those obtained directly from phenylsemicarbazide, so that the assumption that in many cases they represent hydrazi-derivatives falls to the ground (Armstrong and Robertson, T., 1905, **87**, 1272).

Molecular weight measurements show that the hydrazones of ordinary aldehydes and ketones exhibit either no, or but little, tendency to form double molecules, the corresponding carbonyl compounds themselves showing no tendency to the formation of hydrates. The propensity of certain hydrazones, especially those of benzaldehyde, acetophenone, and *iso*cyclic ketones, to pass into azines with loss of hydrazine, is explained by the decomposition of the double molecules in accordance with the scheme:

$$2CR_2\colon N\cdot NH_2 \rightleftharpoons NH_2\cdot NH\cdot CR_2\cdot NH\cdot N\colon CR_2 \rightarrow CR_2\colon N\cdot N\colon CR_2 + N_2H_4.$$

The results described above show that all known hydrazine derivatives of carbonyl compounds have hydrazonic formulæ.

Ethyl oxomalonatehydrazone (compare Neeresheimer, Diss., Munich, 1908) forms colourless crystals, m.p. 80°, b.p. 100°/0·15 mm., and yields benzaldazine when boiled for a day with alcoholic benzaldehyde solution under a reflux condenser. With phenylcarbimide this hydrazone yields *ethyl oxomalonatephenylsemicarbazone*, $C(CO_2Et)_2\colon N\cdot NH\cdot CO\cdot NHPh$, which forms white crystals, m. p. 117°; the *mesoxalic ester* derivative,

$$OH\cdot C(CO_2Et)_2\cdot NH\cdot NH\cdot CO\cdot NHPh,$$

m. p. 126—128°, prepared from ethyl oxomalonate and phenylsemicarbazide, yields the previous compound when boiled in benzene solution with phosphorus pentoxide. *Ethyl oxomalonatedimethylhydrazone*, $C(CO_2Et)_2\colon N\cdot NMe_2$, forms a pale yellow, viscous oil, b. p. 106—108°/0·1 mm.

The interaction of ethyl oxomalonate and hydrazimethane yields a compound, b. p. 90—91°/0·15 mm., which has not the composition of ethyl dimethylhydrazimethanemalonate, and is to be investigated further. Ethyl oxomalonate and benzoylhydrazine yield the *compound*, $OH\cdot C(CO_2Et)_2\cdot NH\cdot NHBz$, m. p. 100°.

Ethyl oxomalonate-p-*tolylhydrazone* forms pale, yellowish-green crystals, m. p. 77°.

Benzaldehyde diphenylacetylhydrazone, $C_{21}H_{18}ON_2$, prepared from diphenylketen and benzaldehydehydrazone, forms crystals, m. p. 196°,

and *benzophenonediphenylacetylhydrazone*, $C_{27}H_{22}ON_2$, has m. p. 151—152°.

Fluorenonephenylsemicarbazone, $C_{20}H_{15}ON_3$, forms crystals, m. p. 222°, and *benzilphenylsemicarbazone*, $C_{21}H_{17}O_2N_3$, has m. p. 167—169°. T. H. P.

Aliphatic Diazo-compounds. XXII. Reduction of Ethyl Diazoacetate. H. STAUDINGER, L. HAMMET, and J. SIEGWART (*Helv. Chim. Acta*, 1921, **4**, 228—238).—Hydrogen sulphide alone acts slowly on ethyl diazoacetate, but in presence of ammonia a liquid reduction product is obtained which was at first considered to be ethyl hydrazi-acetate, $CO_2Et\cdot CH<\begin{matrix}NH\\|\\NH\end{matrix}$. This compound is sparingly soluble in water and changes slowly into a soluble isomeride, this being regarded as ethyl glyoxylatehydrazone, $CO_2Et\cdot CH:N\cdot NH_2$. These constitutions are supported by (1) the normal molecular weight of the original, and the marked association of the final, product in freezing benzene, and (2) the fact that the original compound reacts only slowly with phenylcarbimide (1 mol.) and not at all with diphenylketen, whereas the presumed hydrazone reacts readily and vigorously with both reagents.

In spite of such pronounced differences in behaviour shown by the two compounds, these are found to be, not structurally, but spacially isomeric, the liquid compound being the *syn*- and the other the *anti*-hydrazone. In agreement with the results obtained with ethyl oxomalonatehydrazone, the reactivity of the amino-group is greatly depressed by the proximity of the carboxyl group, this explaining the behaviour towards phenylcarbimide and diphenylketen and also the ability of the anti- and the non-ability of the syn-compound to form double molecules.

Solid ethyl oxomalonatehydrazone combines in itself, to some extent, the properties of the syn- and anti-compounds. Its amino-group is less reactive than that of the syn-compounds, yet the compound associates because the double linking in an ethyl oxomalonate derivative is even more highly unsaturated than that in an ethyl glyoxylate derivative. Otherwise the two stereoisomeric hydrazones behave similarly. They are converted into ethyl glyoxylate and hydrazine by hydrolysis, into ethyl diazoacetate when oxidised by means of mercuric oxide, and into benzaldazine by the action of benzaldehyde; just as with the ethyl oxomalonate derivative (preceding abstract), so also in this case, no mixed ketazine is obtained.

Examination of the two isomeric camphorquinonehydrazones obtained by Forster and Zimmerli (T., 1910, **97**, 2156), shows that the syn-compound, with the lower melting point, does not associate in benzene solution; the anti-compound dissolves only very slightly in benzene. Further, with phenylcarbimide the readily soluble syn-isomeride reacts more rapidly than the anti-compound. Busch, Achterfeldt, and Seufert (A., 1917, i, 228) obtained stereoisomeric aromatic hydrazones of glyoxylic acid which differ markedly in their reactions.

syn-*Ethyl glyoxylatehydrazone*, $CO_2Et\cdot CH:N\cdot NH_2$, is a colourless, odourless, mobile liquid, b. p. 38—40°/0·2 mm., 82° (decomp.)/13 mm. The anti-*isomeride* forms a white, crystalline mass, m. p. 38—38·5°. Both forms are decomposed instantly by concentrated hydrochloric acid, with separation of hydrazine hydrochloride; similarly, the action of dilute sulphuric acid gives hydrazine sulphate.

syn-*Ethyl glyoxylatephenylsemicarbazide*,

$$CO_2Et\cdot CH:N\cdot NH\cdot CO\cdot NHPh,$$

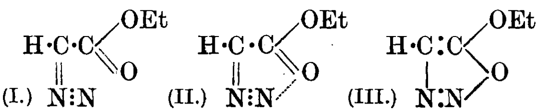
forms colourless crystals, m. p. 128—130°, and the anti-*isomeride*, white crystals, m. p. 176°.

anti-*Ethyl glyoxylatediphenylacetylhydrazone*,

$$CO_2Et\cdot CH:N\cdot NH\cdot CO\cdot CHPh_2,$$

prepared from the *anti*-hydrazone and diphenylketen, forms colourless crystals, m. p. 178°. T. H. P.

Aliphatic Diazo-compounds. XXIII. Formulation of Ethyl Diazoacetate and of Diazo-anhydrides. H. STAUDINGER (*Helv. Chim. Acta*, 1921, **4**, 239—241).—The fact that cautious reduction of ethyl diazoacetate by means of ammonium sulphide yields first only *syn*-ethyl glyoxylatehydrazone indicates either (1) that the diazo-group in the diazo-ester occupies the *syn*-position to the carbethoxy-group (I), or (2) that these groups are united by secondary valencies (II), or (3) that ethyl diazoacetate is a diazo-anhydride, that is, a furodiazole derivative (III) (compare Wolff, Bock, Lorentz, and Trappe, A., 1903, i, 203). That the last of these formulæ is incorrect (compare Schroeter, A., 1909, i, 617; Dimroth, A., 1910, i, 518; Staudinger, A., 1916, i, 847) is shown by the following considerations.



First, diazo-anhydrides, such as benzoylacetyldiazomethane, should exist in isomeric modifications, which is actually not the case. Further, of the corresponding thiazole derivatives, which certainly have ring formulæ, isomeric products are known, these being obtained together from benzoylacetyldiazomethane (Wolff, A., 1912, i, 1028). Again, Mächling's attempts to prepare isomeric methyl ethyl diazomalonates from (1) methyl diazoacetate, carbonyl chloride, and ethyl alcohol, and (2) ethyl diazoacetate, carbonyl chloride, and methyl alcohol, resulted in failure (Diss., Zürich, 1916).

The assumption that all diazo-compounds, including ethyl diazomalonate, the diazo-anhydrides, and the azides, are to be represented by the Angeli-Thiele formulation is supported also by the behaviour towards tertiary phosphines, which react almost equally readily with all these compounds; when heated, the phosphazines dissociate, giving the initial compounds, if the diazo-compounds happen to be sufficiently stable in the hot.

T. H. P.

The Chlorovinylchloroarsines. STANLEY JOSEPH GREEN and THOMAS SLATER PRICE (T., 1921, **119**, 448—452).

Boron Trimethyl and Boron Triethyl. ALFRED STOCK and FRIEDRICH ZEIDLER (*Ber.*, 1921, **54**, [*B*], 531—541).—Boron trimethyl and boron triethyl have been described by Frankland (this Journal, 1862, **15**, 373, 367); the molecular weight of the former, as deduced from determinations of the vapour density, is in good agreement with the formula BMe_3, whilst the ethyl derivative appears to be slightly polymerised, particularly at the lower temperatures; the behaviour of these substances is thus in striking contrast with that of the boron hydrides, the simplest representative of which has the formula B_2H_6. Re-examination of the alkyl compounds has, however, very largely confirmed Frankland's results.

The manipulation of the substances, which are very sensitive to moisture and grease, was effected by the author's vacuum process, several new applications of which are described and illustrated in the original; the control of the parity is effected by measurement of the tension.

Boron trimethyl is obtained by the action of boron chloride and zinc methyl in the gaseous phase, the reaction being moderated by cooling or by working under suitably diminished pressure. It has m. p. $-161\cdot5°$, D^{-100} 0·625 (as liquid). The following tensions are recorded: 1 mm., $-118°$; 2 mm., $-113°$; 3 mm., $-108°$; 4 mm., $-103°$; 6 mm., $-98°$; 10 mm., $-93\cdot3°$; 15 mm., $-88\cdot4°$; 21 mm., $-83\cdot5°$; 32 mm., $-78\cdot4°$; 43 mm., $-73\cdot8°$; 60 mm., $-68\cdot9°$; 82 mm., $-64\cdot1°$; 113 mm., $-59\cdot2°$; 147 mm., $-54\cdot3°$; 192 mm., $-49\cdot4°$; 253 mm., $-44\cdot5°$; 319 mm., $-39\cdot6°$; 406 mm., $-34\cdot6°$; 511 mm., $-29\cdot7°$; 759 mm., $-20\cdot2°$. The pure substance inflames spontaneously on contact with air. It is very stable at the ordinary temperature. The effect of varying pressure and temperature on the gaseous density has been fully investigated (a special form of differential tensimeter for the latter observations is depicted); between the temperatures, $-25°$ and $+100°$, the density corresponds exactly with the formula BMe_3.

Boron triethyl, prepared from zinc ethyl and boron trichloride, has m. p. $-92\cdot9°$, b. p. 95°, D^{23} 0·6931, tension at 0° 12·5 mm. It undergoes slow decomposition when heated, yielding small amounts of ethane and hydrogen; this action is but little influenced by water, and is accelerated by alkali, and thus is possibly to be ascribed to the effect of the alkali of the glass. Contrary to Frankland's observation, the vapour density close to the boiling point and even at lower temperatures corresponds almost exactly with the simple formula BEt_3; appreciable polymerisation cannot be detected. The diminution of density with increase of temperature recorded by Frankland is probably due to the slow thermal decomposition of the substance which had been overlooked previously.

Boron trimethylammine, BMe_3NH_3, obtained by the union of boron trimethyl and ammonia, forms many-sided, highly refractive volatile crystals, m. p. 56°, b. p. 110°, and has the tensions 1·0 mm. at 0°, 1·8 mm. at 5·6°, 2·0 mm. at 10°, 3·2 mm. at 15·2°, 11·0 mm. at 31·2°, and 16·5 mm. at 36·9°. The vapour density has been measured over the range of temperature 25·0° to 70·0°, and the

results show that at the lower temperatures a moderate proportion (about 10% at 25—30°) of undissociated ammine can exist in the gaseous state. Determinations of the molecular weight in benzene solution by the cryoscopic method indicate that the ammine is practically undissociated under these conditions; the solution is stable towards air, does not smell of ammonia, but has a faint odour of boron trimethyl. H. W.

The Constitution of the Mercury Compounds of Carbon Monoxide and of Ethylene. II. WILHELM MANCHOT (*Ber.*, 1921, **54**, [*B*], 571—574).—A further contribution to the controversy on this subject (compare Manchot, A., 1920, i, 519; Schoeller, Schrauth, and Essers, A., 1913, i, 1162; 1920, i, 225; Schoeller, this vol., i, 16). H. W.

Some Derivatives of Thujamenthone. MARCEL GODCHOT (*Compt. rend.*, 1921, **172**, 686—688).—Thujamenthone, when passed with hydrogen over reduced nickel at 280°, is converted into 1 : 2-dimethyl-3-*iso*propyl*cyclo*pentane. When magnesium methyl iodide acts on thujamenthone, a mixture of two isomeric 1 : 2 : 3-*trimethyl*-4-iso*propyl*cyclo*pentenes*, b. p. 159—165°, D^{13} 0·8113; n_D^{13} 1·4518, is obtained, and these, on hydrogenation by reduced nickel at 180°, yield 1 : 2 : 3-*trimethyl*-4-iso*propyl*cyclo*pentane*, b. p. 157—158°; D^{13} 0·7833; n_D^{13} 1·4326. Using the method of condensation of ketones by means of calcium hydride (compare A., 1919, i, 447), thujamenthone yielded 2 : 3-*dimethyl*-4-iso*propyl*cyclo*pentylidene*-3 : 4-*dimethyl*-2-iso*propyl*cyclo*pentan*-5-*one*,

$$\begin{array}{l}CH(CHMe_2)\cdot CH_2 \\ CHMe\text{——}CHMe\end{array}\!\!>C{:}C<\!\!\begin{array}{l}CO\text{——}CHMe \\ CH(CHMe_2)\end{array}\!\!>CHMe,$$

b. p. 182—184°/10 mm.; D^{15} 0·9123; n_D^{15} 1·4825, giving an oily *oxime*. W. G.

Considerations on the Inner Constitution of Benzene and certain Heterocyclic Nuclei. G. CIAMICIAN and R. CIUSA (*Atti R. Accad. Lincei*, 1921, [*V*], **30**, i, 72—74).—On the basis of the results obtained by Angeli (A., 1917, i, 452; 1920, i, 665), various conclusions are drawn concerning the arrangement of the valencies in the molecules of benzene, pyridine, pyrrole, and thiophen. T. H. P.

Oxidation of Aromatic Hydrocarbons under Pressure. HANS SCHRADER (*Ges. Abhand. Kennt. Kohle*, 1920, **4**, 310—341; from *Chem. Zentr.*, 1921, i, 537).—The autoxidation of aromatic hydrocarbons by air under increased pressure and in the presence of aqueous alkaline solutions takes place so readily at a comparatively low temperature (about 200°) that it is possible to obtain oxidation products in considerable quantity in the course of a few hours. In the series, benzene, naphthalene, anthracene, the autoxidisability increases with increasing number of nuclei; with the homologues of benzene, it increases with the number of aliphatic groups. Benzene and chlorobenzene are not noticeably affected at 210°, but action begins to be obvious at 260°. Naphthalene is

scarcely changed at 210°, but is markedly oxidised, mainly to phthalic acid, at 260°; anthracene is distinctly attacked at 210°, and completely changed at 260°, being transformed mainly into anthraquinone and smaller amounts of naphthalene-2 : 3-dicarboxylic and phthalic acids. With the homologues of benzene, the chief reaction consists in the complete or partial conversion of the aliphatic residues into carboxyl groups. Small amounts of benzoic acid are produced from toluene or ethylbenzene at 210°. The xylenes are more readily changed and pass into the corresponding toluic and phthalic acids. *p*-Cymene is still more readily oxidised, yielding, amongst other products, cumic, toluic, and terephthalic acids. The three chlorotoluenes are noticeably more stable than the parent substance, but, at 260°, are converted into the corresponding chlorobenzoic acids. Under the experimental conditions, all the aromatic hydrocarbons are oxidised to oxalic, acetic, formic, and carbonic acids to a greater or less extent. The intermediate formation of aldehydes is established. The mechanism of the oxidative process is discussed and a review is given of the literature on the oxidation of aromatic hydrocarbons by air or gaseous oxygen. The phenomena of autoxidation are of considerable importance in connexion with the use of aromatic hydrocarbons in internal combustion engines. The temperature of ignition, autoxidisability, and stability of a compound are closely related to one another. H. W.

The Friedel-Crafts' Reaction. II. Migration of Halogen Atoms in the Benzene Nucleus. MAURICE COPISAROW (T., 1921, **119**, 442—447).

The Nitrotoluenes. VI. The Three-component System: *o*-Nitrotoluene-*p*-Nitrotoluene-2:4-Dinitrotoluene. JAMES M. BELL and EDWARD B. GORDON (*J. Ind. Eng. Chem.*, 1921, **13**, 307—308).—This system has been investigated by the methods previously described (A., 1920, i, 152, 153). Since two forms of *o*-nitrotoluene exist (this vol., i, 234), the system should give two diagrams, with this component in its stable and metastable modifications, the two being identical except where the *o*-nitrotoluene is in the solid phase; neither binary eutectic containing *o*-nitrotoluene was, however, found in presence of the metastable form. The ternary eutectic temperature, — 20·1°, corresponds with 62, 19, and 19% of *o*-nitrotoluene, *m*-nitrotoluene, and 2 : 4-dinitrotoluene. T. H. P.

The Nitrotoluenes. VII. The Three-component System: *p*-Nitrotoluene - *o*-Nitrotoluene - 2 : 4 : 6-Trinitrotoluene. JAMES M. BELL and FLETCHER H. SPRY (*J. Ind. Eng. Chem.*, 1921, **13**, 308).—The three binary systems of these components (A., 1920, i, 152; this vol., i, 234) form no compounds, the freezing-point curve consisting in each case of two lines intersecting in a eutectic point. For the ternary system, the eutectic temperature is — 19·5° and the eutectic composition 65·5, 19·5, and 15% of *o*-nitrotoluene, *p*-nitrotoluene, and the trinitrotoluene respectively. T. H. P.

Halogenation. XX. The Replacement of Sulphonic Acid Groups by Halogens. RASIK LAL DATTA and JAGADISH CHANDRA BHOUMIK (*J. Amer. Chem. Soc.*, 1921, **43**, 303—315).—Previous work (A., 1920, i, 157) has been extended, and it is now shown that the replacement of sulphonic groups in aromatic compounds by chlorine or bromine takes place generally and may occur with iodine under special conditions. As previously indicated, more halogen atoms usually enter the ring at the same time with the formation of higher halogen derivatives. The method may be used for determining the constitution of halogen derivatives prepared from known sulphonic acids.

Groups already present in the nucleus exert a great influence upon the replacement, and certain general rules have been observed. The replacement of sulphonic acid groups by bromine takes place readily at ordinary temperatures in the case of compounds with one or more hydroxyl groups attached to the nucleus, although if there are two hydroxyl groups ortho to one another oxidation often occurs with bromine. The presence of an amino-group similarly facilitates the replacement. On the other hand, the presence of nitro-groups retards the replacement. In the case of hydroxycarboxylic acids, the sulphonic group is replaced by halogens, but at the same time the carboxyl group is detached and hydroxyhaloid derivatives are formed. This is exactly comparable with the action of nitrous gases under similar conditions (A., 1920, i, 158). The presence of halogen atoms makes the replacement difficult. Thus bromobenzenesulphonic acid gives with great difficulty the corresponding dibromobenzene.

The presence of one or more alkyl groups also renders the displacement difficult, but the effect is variable. Thus in the case of toluenesulphonic acid the replacement cannot be effected by chlorine, and only with very great difficulty by bromine. With the xylenes and mesitylene, the replacement of the sulphonic group is slightly easier. In the case of the benzenesulphonic acid group, the replacement does not take place at all.

The detachment of the sulphonic group by halogens or nitrous gases takes place more easily in the case of a monosulphonic acid than in that of a di- or tri-sulphonic acid. In these replacements, instead of using free bromine, it is better to use a mixture of alkali bromide and bromate, as the bromine is liberated very gradually with simultaneous substitution, and the chances of charring and secondary reactions are eliminated altogether. A mixture of chloride and chlorate gives no better results than free chlorine itself, but a mixture of iodide and iodate will in some cases effect a replacement which free iodine itself fails to do.

Numerous examples are given illustrative of this reaction as applied to different types of compounds, and some new haloid compounds are described. *o*-4-Xylenolsulphonic acid gives a quantitative yield of 3 : 6-*dibromo*-o-4-*xylenol*, m. p. 106°, but a poor yield of a (??)-*dichloro*-o-4-*xylenol*, b. p. 232°. *p*-2-Xylenolsulphonic acid gave (??)-*dichloro*-p-2-*xylenol*, m. p. 84°.

W. G.

Preparation of *p*-Nitrotoluene-*o*-sulphonic Acid from Cymene. S. V. HINTIKKA (*Ann. Acad. Sci. Fennicae*, 1917, [*A*], **10**, 1—4; from *Chem. Zentr.*, 1921, i, 357).—In the preparation of nitrocymenesulphonic acid by the method of Errera (A., 1891, i, 1066), cymene is treated successively with sulphuric and nitric acids, diluted, and neutralised with barium carbonate. The mother liquor after the crystallisation of the barium salt of nitrocymene-*o*-sulphonic acid gives, with the required quantity of sulphuric acid, prisms of *p*-nitrotoluene-*o*-sulphonic acid, $SO_3H{\cdot}C_6H_3Me{\cdot}NO_2$,aq., m. p. 133·5°. *p*-Aminotoluene-*o*-sulphonic acid,

$$SO_3H{\cdot}C_6H_3Me{\cdot}NH_2,H_2O,$$

forms rhombohedra soluble in water. Nitrotoluenesulphonic acid gives, on boiling with sodium hydroxide and a suitable reducing agent, the well-known stilbene colours. Diaminostilbenedisulphonic acid may also be obtained from it. G. W. R.

The Condensation of Acetylene with Benzene and its Derivatives in the Presence of Aluminium Chloride. OTTO W. COOK and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1921, **43**, 334—340).—Contrary to the results of Varet and Vienne (A., 1886, 806, 1375), the authors find that the normal course of the action of acetylene on benzene in the presence of aluminium chloride is the union of two molecules of benzene with one molecule of acetylene to form αα-diphenylethane, which in part combines with more acetylene to yield an anthracene derivative.

Benzene itself yields αα-diphenylethane and 9:10-dimethylanthracene hydride in almost equal proportions, but only a trace of styrene. Toluene gives *as*-di-*p*-tolylethane, 2:7-dimethylanthracene, and some 2:6-dimethylanthracene and β-methylanthracene with xylene, mesitylene, and ψ-cumene as products of side reactions. Chlorobenzene gives *di*-p-*chloro*-as-*diphenylethane*, $C_6N_4Cl{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl$, b. p. 210—212°/30 mm. and 319—321°/760 mm., and another material not identified. Dimethylaniline gives a small amount of di-*p*-dimethylamino-*as*-diphenylethane. Nitrobenzene, phenyl acetate, phenol, methyl benzoate, and aniline undergo preliminary reaction or condensation with aluminium chloride, and do not act further. W. G.

Additive Power of certain Styrene Derivatives. S. REICH, R. VAN WIJCK, and C. WAELLE (*Helv. Chim. Acta*, 1921, **4**, 242—249. Compare this vol., i, 27).—Experiments made with the following *s*-derivatives of styrene: methyl-, ethyl-, dimethyl-, *iso*propyl-, *iso*butyl-, methyl-*n*-butyl-, *n*-hexyl-, and *cyclo*hexylstyrenes and benzylidene*cyclo*hexane show that the capacity of styrene to combine with bromine is increased slightly by replacement of the methylenic hydrogen atoms by alkyl radicles, and is greater when two atoms than when one atom of hydrogen is replaced. Elongation of the direct chain of the substituting alkyl lowers the additive power, and replacement of the direct chain by a branched chain appears to act in the same way. A closed-chain substituent gives a greater additive capacity than the corresponding open-chain substituent.

Experiments with stilbene, *o*- and *p*-methoxystilbenes, chloro- and bromo-styrenes, cinnamonitrile, cinnamic acid, methyl and phenyl cinnamates, bromo- and phenyl-cinnamic acids, and methyl and phenyl phenylcinnamates show that replacement of an aliphatic radicle by phenyl diminishes considerably the additive power, whilst replacement of a phenylic hydrogen by methoxyl increases this power. Introduction of a halogen lowers the additive power, although far less so than that of a cyanogen group, the influence of which is approached by the influence of the carboxyl group. Double substitution by these depressive groups, that is, the halogens, cyanogen, and carboxyl, almost entirely destroys the additive power.

The alkyl derivatives of styrene employed were prepared by a method involving the three successive stages: (1) Action of benzaldehyde or phenylacetaldehyde on organo-magnesium compounds, $CH_2R\cdot MgCl$, giving secondary alcohols, $OH\cdot CHPh\cdot CH_2R$ or $CH_2Ph\cdot CH(OH)\cdot CH_2R$. (2) Treatment of the alcohol with hydrogen chloride at 0°, yielding the chloro-derivative, $CHPhCl\cdot CH_2R$ or $CH_2Ph\cdot CHCl\cdot CH_2R$, and (3) treatment of the latter with pyridine at 125°, the styrene hydrocarbon, $CHPh{:}CHR$ or $CHPh{:}CH\cdot CH_2R$, being thus obtained. The following are new compounds:

β-iso*Butylstyrene* [*α-Phenyl-δ-methyl-Δ^{α}-pentene*], $CHPh{:}CH\cdot CH_2Pr^{\beta}$, is a mobile liquid with a pleasant odour, b. p. 107—109°/11 mm., and was prepared by way of *phenyl*iso*amylcarbinol*,

$$OH\cdot CHPh\cdot CH_2\cdot CH_2Pr^{\beta},$$

which is a colourless liquid, b. p. 132°/8 mm.

α-Phenyl-β-methyl-Δ^{α}-hexene, $CHPh{:}CMe\cdot CH_2Pr^{\alpha}$, is a mobile liquid, b. p. 114—116°/12 mm., D^{17} 0·8974, *n* 1·51505, with the odour of fir cones, and was obtained by the action of sulphuric acid on *phenyl*iso*hexylcarbinol*, $OH\cdot CHPh\cdot CHMe\cdot CH_2Pr^{\alpha}$, which is a somewhat oily liquid, b. p. 144—145°/13 mm., D^{17} 0·9574, *n* 1·50310.

α-Phenyl-Δ^{α}-octene, $CHPh{:}CH\cdot[CH_2]_5\cdot CH_3$, a liquid, b. p. 136—138°/13 mm., D^{17} 0·9063, *n* 1·50728, was obtained by the action of sulphuric acid on *benzylhexylcarbinol*, $C_{14}H_{22}O$, which is a colourless, oily liquid with a faint, pleasing odour, b. p. 163—165°/13 mm., D^{17} 0·9348, *n* 1·50151.

β-cyclo*Hexylstyrene*, $CHPh{:}CH\cdot C_6H_{11}$, is a colourless liquid of agreeable odour, b. p. 145—147°/14 mm., D^{17} 0·9595, *n* 1·53701, it yields benzoic and *cyclo*hexanecarboxylic acids when oxidised by means of permanganate, and was prepared by the action of sulphuric acid on *benzyl*cyclo*hexylcarbinol*, $C_{14}H_{22}O$, which forms crystals, m. p. 60°, b. p. 175—177°/18 mm.

*Benzylidene*cyclo*hexane*, $CHPh{:}C_6H_{10}$, obtained by the action of sulphuric acid on phenyl*cyclo*hexylcarbinol (compare Sabatier and Mailhe, A., 1904, i, 810), is a colourless liquid with an odour of aniseed, b. p. 122—123°/11 mm., D^{17} 0·9640, *n* 1·53950.

T. H. P.

Preparation of Tetrahydronaphthalene. AKTIEN GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.P. 298541, 298553, 301275; from *Chem. Zentr.*, 1921, ii, 559).—A mixture of naphthalene

vapour and hydrogen is passed over a mixture of nickel and copper oxides without employment of increased pressure; a smooth formation of tetrahydronaphthalene is observed at 140—150°. The second patent claims the use of mixtures of the oxides of manganese, nickel, and copper, including such as are mainly composed of the first-named. In the third patent, catalysts are cited in which the oxides of nickel, copper, or manganese are completely or partly replaced by an oxide of the rare earth metals, particularly thorium or cerium oxide. H. W.

Electrolytic Reactions of Naphthalene and its Derivatives. I. Electrolytic Oxidation of Naphthalene. KASHICHI ONO (*J. Chem. Soc. Japan*, 1921, **42**, 38—66).—Naphthalene is electrolytically oxidised to α-naphthaquinone, with the formation of small quantities of phthalic acid and dark brown, resinous matter, in acid solution, using lead peroxide and platinum as the positive pole, but not in alkaline solution. The author studied the effects of the concentration of the acid used, the current density, the reaction temperature, the electric quantity, and the catalysts used as oxygen carriers. The presence of α-naphthol in the electrolytic solution was observed and a red compound, which seems to be a compound of α-naphthol and naphthaquinone, produced in the electrolytic oxidation, was obtained by steam distillation of the solution of α-naphthol. The dark brown, resinous substance contains phenolic hydroxyl groups and yields (*a*) phthalic acid and an insoluble black substance when fused with potassium hydroxide; (*b*) a large quantity of phthalic acid on oxidation with alkaline potassium permanganate; (*c*) αα- and ββ-dinaphthyls by distillation with zinc dust; and (*d*) α-naphthaquinone, ββ-dinaphthyl-α-diquinone and violet-brown substances when acted on by nitric acid (compare Stenhouse and Groves, *Annalen*, 1879, **194**, 206). K. K.

Influence of Sodium Chloride and Sodium Sulphate on the Solubility in Water of Sodium β-Naphthalenesulphonate. W. TERNENT COOKE (*J. Soc. Chem. Ind.*, 1921, **40**, 56).—The solubility of sodium β-naphthalenesulphonate has been determined at 25°, 30°, 40°, 50°, and 65° in solutions of sodium chloride and sodium sulphate respectively. The results are expressed in curves, which show that the solubility of the sulphonate is reduced almost to zero when the concentration of the sodium salt reaches about 10 grams in 100 grams of solution. It is shown that at 25° the presence of the sulphonate has practically no influence on the solubility of sodium sulphate. J. F. S.

Formation of Anthracene from Benzene and Ethylene. J. E. ZANETTI and M. KANDELL (*J. Ind. Eng. Chem.*, 1921, **13**, 208—211).—The formation of anthracene from benzene and ethylene was studied, the mixture of benzene vapour and ethylene being passed at ordinary pressure through a quartz tube heated at 800° to 1000°. The optimum temperature was found to be 925°, the yield of anthracene being 0·675% of the weight of benzene decom-

posed. Above this temperature, the formation of carbon increased rapidly whilst that of anthracene decreased and ceased at 1000°.
W. P. S.

The Fluorene Series. K. STAHRFOSS (*Bull. Soc. chim.*, 1921, [iv], **29**, 142—152).—When 2 : 7-dibromofluorene is warmed with alcoholic sodium hydroxide, 2 : 2′ : 7 : 7′-*tetrabromo-αδ-bisdiphenylene-$\Delta^{\alpha\gamma}$-butadiene* is obtained, crystallising from aniline in red needles, and very stable to heat and indifferent to chemical reagents. It is acted on by strong nitric acid in acetic acid solution in the presence of a little sulphuric acid to give what is probably a tetranitro-derivative. If dibromofluorene and 1-chloro-2 : 4-dinitrobenzene are mixed in alcoholic solution and alcoholic potassium hydroxide is added, a deep blue colour is obtained which slowly fades on keeping or disappears instantly on acidifying the solution. It is probable that condensation takes place with the formation of the compound, $\begin{matrix} C_6H_3Br \\ | \\ C_6H_3Br \end{matrix}\!\!>CH\cdot C_6H_3(NO_2)_2$. Dinitrofluorene behaves in a similar manner. It is probable that the blue colour is due to a quinonoid form of the compound, a similar colour reaction, this time red, occurring with dibromofluorene and *p*-aminophenol.

There is some indication that the introduction of negative groups into the diphenylene complex of the fluorene augments the acid character of the methylene group.
W. G.

The Binary System: Aniline–Acetic Acid. EDMUND ARTHUR O'CONNOR (T., 1921, **119**, 400—403).

Optical Investigations of the Constitution of Aromatic Amines. H. LEY and G. PFEIFFER (*Ber.*, 1921, **54**, [*B*], 363—378; Compare A., 1917, i, 261; 1919, ii, 178).—It has been shown previously that the introduction of the methyl group into certain unsaturated compounds with a conjugated system has a hypsochromic effect and that this is also occasionally observed with the typical auxochromic alkoxy-groups. This behaviour, which has only been noticed previously with unsaturated systems with an open chain, is now found to be exhibited by certain derivatives of benzene and in particular by dimethylaniline after introduction of certain groups; these ortho-substituted dimethylanilines are found to be abnormal in other physical and chemical properties.

Dimethyl-, diethyl-, dipropyl- and diamyl-anilines exhibit closely similar absorption curves; the introduction of a methyl group into the para- or meta-position does not greatly alter the character of the absorption, which, however, becomes markedly different when the group is placed in the ortho-position. Similar observations are recorded with the dimethylxylidines; if the ortho-positions to the dimethylamino-group remain unoccupied, the absorption resembles closely that of dimethylaniline, but anomalies are observed when one or particularly when both positions are occupied by methyl-groups. *o*- and *p*-Chlorodimethylanilines and *o*- and *p*-methoxydimethylanilines show the same difference in behaviour,

which, however, is not observed with the nitrodimethylanilines. The peculiarity in the behaviour of the ortho-substituted compounds extends to the products formed with polynitro-derivatives; thus dimethyl-*p*-toluidine and dimethyl-*m*-toluidine yield blackish-violet and shining black derivatives with trinitrobenzene, whereas dimethyl-*o*-toluidine gives a yellowish-brown additive compound. The molecular refraction and dispersion of ortho-substituted dimethylanilines is also found to be abnormal.

The following hypothesis is provisionally advanced in explanation of these observations. The benzene ring does not comprise a completely neutral conjugated system, but each carbon atom has a certain amount of residual affinity which is altered (generally increased) by substituents. The introduction of particularly reactive, unsaturated groups, such as $\cdot NMe_2$, increases the amount of the partial valency at each carbon atom, since the whole system is composite; the benzene complex bonds become thereby more active, and approximate somewhat to the olefinic bond. The change of state is shown in the complete alteration of the absorption curve of the hydrocarbon and the notable displacement of the absorption towards the red, as also in the increase in the refraction and dispersion values. Substituents in the ortho-position can partly neutralise the reactivity of the complex bonds, so that the amount of partial valency of each carbon atom is again diminished. Possibly, also, the increase in size of the substituents is a factor.

The introduction of a substituent into the ortho-position in a primary or secondary amine does not cause the same anomalies as in the case of a tertiary amine.

The following physical constants are recorded. The tertiary amines were prepared, when possible, by methylating the primary amine with methyl iodide to the quaternary iodide and conversion into the quaternary base by means of silver oxide and subsequent distillation of the base; the other tertiary amines were purified by treatment with acetic anhydride. The observations were made at 20°. Dimethylaniline, b. p. 194—194·6°/752 mm., D_4^{20} 0·9563, n_α 1·55189, n_D 1·55869, n_β 1·57654, n_γ 1·59333; dimethyl-*o*-toluidine, b. p. 184·6—185·4°/762 mm., D_4^{20} 0·9287, n_α 1·52032, n_D 1·52548, n_β 1·53872, n_γ 1·55033 (*compound* with trinitrobenzene, yellowish-brown, rhombic plates, m. p. *ca.* 113°); methyl-*o*-toluidine, b. p. 207—208°, D_4^{20} 0·9769, n_α 1·55854, n_D 1·56488, n_β 1·58149; dimethyl-*m*-toluidine, b. p. 211·5—212·5°/761 mm., D_4^{20} 0·9410, n_α 1·54288, n_D 1·54917, n_β 1·56582, n_γ 1·58150 (*compound* with trinitrobenzene, shining black prisms, m. p. 107—108°); dimethyl-*p*-toluidine, b. p. 209·6—210·6°, D_4^{20} 0·9366, n_α 1·54022, n_D 1·54603, n_β 1·56357, n_γ 1·57969 (*compound* with trinitrobenzene, long, blackish-violet needles); *m*-2-xylidine, b. p. 215·8—216·4°/749 mm., D_4^{20} 0·9796, n_α 1·55524, n_D 1·56116, n_β 1·57631, n_γ 1·59026; *m*-2-dimethylxylidine, b. p. 195—196·2°/749 mm., D_4^{20} 0·9147, n_α 1·50859, n_D 1·51310, n_β 1·52488, n_γ 1·53649 (*compound* with trinitrobenzene, scarlet platelets, m. p. 108°); *m*-4-dimethylxylidine, b. p. 203—205°, D_4^{20} 0·9164, n_α 1·51571, n_D 1·52011, n_β 1·53282, n_γ 1·54486 (*compound* with trinitrobenzene, brown platelets, m. p.

114°); *o*-4-dimethylxylidine, b. p. 231·8—232·2°, D_4^{20} 0·9386, n_α 1·54190, n_D 1·54810, n_β 1·56425, n_γ 1·57996 (*compound* with trinitrobenzene, short, blackish-violet needles, m. p. 103°); *o*-chlorodimethylaniline, b. p. 207·5—208·5°, D_4^{20} 1·1067, n_α 1·54722, n_D 1·55278, n_β 1·56776, n_γ 1·58130 (compound with trinitrobenzene, large, brown plates, m. p. 110—111°); *p*-chlorodimethylaniline, m. p. 35·5° (*compound* with trinitrobenzene, blackish-brown needles, m. p. 124°); *o*-nitrodimethylaniline, b. p. 154°/24 mm., D_4^{20} 1·1794, n_D 1·61021 (*compound* with trinitrobenzene, long, yellowish-red rhombic platelets, m. p. 112°); *p*-nitrodimethylaniline, m. p. 163° (*compound* with trinitrobenzene, yellow platelets).

H. W.

Derivatives of *p*-Nitrobenzaldehyde. ALEXANDER LOWY and CHARLES G. KING (*J. Amer. Chem. Soc.*, 1921, **43**, 625—627).—By the condensation of *p*-nitrobenzaldehyde with aromatic amines there were obtained :—p-*Nitrobenzylidene*-o-*phenetidine*, yellow plates, m. p. 81°. p-*Nitrobenzylidene*-p-*bromoaniline*, yellow needles, m. p. 160·5°. p-*Nitrobenzylidene*-o-*toluidine*, yellow plates, m. p. 89°. p-*Nitrobenzylidene*-p-*toluidine*, yellow needles, m. p. 122·5°. p-*Nitrobenzylidene*-m : 4-*xylidine*, yellow needles, m. p. 88·5°. p-*Nitrobenzylidene*-m-*nitro*-p-*toluidine*, yellow needles, m. p. 161°. p-*Nitrobenzylidene*-p-*nitroaniline*, yellow needles, m. p. 198·5°. p-*Nitrobenzylidene*-m-*nitroaniline*, yellow needles, m. p. 152°. 2 : 4 : 6-Tribromoaniline did not condense with the aldehyde.

The above products, in contrast to those from 2 : 4-dinitrobenzaldehyde, and 2 : 4 : 6-trinitrobenzaldehyde (A., 1920, i, 440, and following abstracts) are stable towards sunlight. J. K.

Derivatives of 2 : 4-Dinitrobenzaldehyde. II. ALEXANDER LOWY and THOMAS B. DOWNEY (*J. Amer. Chem. Soc.*, 1921, **43**, 346—348. Compare A., 1920, i, 440).—Further condensation products, as follows, are described. 2 : 4-*Dinitrobenzylidene*-p-*bromoaniline*, m. p. 162·5°; 2 : 4-*dinitrobenzylidene*-2 : 4 : 6-*tribromoaniline*, m. p. 185°; 2 : 4-*dinitrobenzylidene*-o-*nitroaniline*, m. p. 174·5°; 2 : 4-*dinitrobenzylidene*-m-*nitroaniline*, m. p. 138°; 2 : 4-*dinitrobenzylidene*-p-*nitroaniline*, m. p. 169·5°; 2 : 4-*dinitrobenzylidene*-o-*phenetidine*, m. p. 141·5°; 2 : 4-*dinitrobenzylidene*-o-*anisidine*, m. p. 140°, and 2 : 4-*dinitrobenzylidene*-p-*anisidine*, m. p. 129°. W. G.

Derivatives of 2 : 4 : 6-Trinitrobenzaldehyde. ALEXANDER LOWY and EMIL HAROLD BALZ (*J. Amer. Chem. Soc.*, 1921, **43**, 341—346).—A number of condensation products of 2 : 4 : 6-trinitrobenzaldehyde with aromatic amines are described, and in some cases the intermediate additive compounds were isolated.

2 : 4 : 6-Trinitrobenzylideneaniline, m. p. 162°, described by Sachs and Everding (A., 1903, i, 425) was obtained in alcoholic solution, but in acetic acid solution an *isomeride*, m. p. 220°, was obtained.

2 : 4 : 6-*Trinitro-α-hydroxybenzyl*-o-*toluidine*,

$C_6H_2(NO_3)_2 \cdot CH(OH) \cdot NH \cdot C_6H_4Me$,

m. p. 106°; 2 : 4 : 6-*trinitrobenzylidene*-o-*toluidine*,

$C_6H_2(NO_2)_3 \cdot CH{:}N \cdot C_6H_4Me$,

m. p. 177°; 2 : 4 : 6-*trinitro-α-hydroxybenzyl-β-naphthylamine*; 2 : 4 : 6-*trinitrobenzylidene-β-naphthylamine*, m. p. 192°; 2 : 4 : 6-*trinitrobenzyl-α-hydroxy-α-naphthylamine*; 2 : 4 : 6-*trinitrobenzylidene-α-naphthylamine*, m. p. 242°; 2 : 4 : 6-*trinitrobenzylidene*-p-*toluidine*, m. p. 179·5°; 2 : 4 : 6-*trinitrobenzylidene*-m-*toluidine*, m. p. 173·5°; 2 : 4 : 6-*trinitrobenzylidene*-m-4-*xylidine*, m. p. 203°; 2 : 4 : 6-*trinitrobenzylidene*-p-*aminoazobenzene*, m. p. 189°; 2 : 4 : 6-*trinitrobenzylidene*-p-*aminophenol*, m. p. 179°; 2 : 4 : 6-*trinitrobenzylidene*-o-*aminobenzoic acid*, m. p. 146°; 2 : 4 : 6-*trinitrobenzaldehydediphenylamine*, m. p. 102°.

The intermediate products were converted into the condensation products when heated or when treated with acetic acid. By the introduction of numerous modifications into the method of Sachs and Everding (*loc. cit.*) for the preparation of 2 : 4 : 6-trinitrobenzaldehyde from trinitrotoluene the yield was quadrupled.

W. G.

Melting Point of Diphenylamine. HOMER ROGERS, W. C. HOLMES, and W. L. LINDSAY (*J. Ind. Eng. Chem.*, 1921, **13**, 314—316).—Carefully purified diphenylamine has m. p. 53·0°, the value 54·0°, generally quoted in standard reference books hence being erroneous. T. H. P.

Chloro-iodo- and Iodoso-derivatives. A. PIERONI (*Gazzetta*, 1921, **51**, i, 47—48).—In pyridine solution, aniline and phenyl iododichloride interact according to the equation $3C_6H_5Cl_2I + NH_2Ph = 2HCl + C_6H_5 \cdot NCl(C_6H_5ClI)_3$. The resulting *compound* forms grey, lamellar crystals of pleasant odour, recalling that of anethole, m. p. 56°. The residual product of the reaction insoluble in ether is blackish-violet, dissolves largely in alcohol giving an intensely violet solution, undergoes change without fusion at about 171°, and contains both chlorine and iodine. T. H. P.

Rôle of Mercuric Nitrate in the "Catalysed" Nitration of Aromatic Substances. I. TENNEY L. DAVIS, D. E. WORRALL, N. L. DRAKE, R. W. HELMKAMP, and A. M. YOUNG (*J. Amer. Chem. Soc.*, 1921, **43**, 594—607).—The yield of picric acid from the action of nitric acid on benzene in presence of mercuric nitrate (Wolffenstein and Boeters, A., 1908, i, 629) is augmented to 50% by weight of the benzene employed by increasing the proportion of nitric acid. *o*-Nitrophenol could not be detected among the products (compare Wolffenstein and Boeters). Nitrobenzenes are not intermediate products, since 2 : 4-dinitrophenol may be obtained, unaccompanied by nitrobenzene, by the use of 10% nitric acid, and beyond a certain concentration of acid, for example, 70%, the yield of picric acid is poor. Further, mono-, di-, and trinitrobenzenes are not convertible into picric acid by nitric acid and mercuric nitrate. Sulphuric acid almost inhibits the formation

of picric acid. The reaction appears to proceed by way of a black intermediate product, containing mercury, which may be isolated from the very dark acid layer, and burns with intumescence, deflagrates on heating, and yields oxides of nitrogen with dinitrophenol when warmed with nitric acid. In this way probably the hydroxyl group and at least one nitro-group are introduced simultaneously. Nitrogen peroxide is the gaseous product of the reaction proper, but is eventually replaced by nitric oxide, due to oxidation of picric acid. Toluene, chlorobenzene, and naphthalene respectively yield trinitro-*m*-cresol, trinitro-*m*-chlorophenol, and nitronaphthols under similar conditions. J. K.

Solubility. IV. Ammines of Salts of Picric Acid and of *p*-Dichlorobenzenesulphonic Acid. FRITZ EPHRAIM (*Ber.*, 1921, **54**, [*B*], 402—406. Compare this vol. ii, 305).—Picric acid gives thick, crystalline precipitates with ammines frequently even in very dilute solution. Hexamminocobaltichloride, chloropentamminocobaltichloride and carbonatotetramminocobaltinitrate give slender *needles*, a heavy *precipitate* and slender prismatic aggregates respectively, whereas *trans*-dinitrotetramminocobaltichloride does not give a precipitate. The following picrates of ammines of uni- and bi-valent metals have been analysed: *nickel* salt, $[C_6H_2(NO_2)_3O]_2[Ni(NH_3)_5(H_2O)_3]$, yellow, microscopic needles, which, at 110°, is converted into the *compound*,

$$[C_6H_2(NO_2)_3O]_2[Ni(NH_3)_5H_2O]:$$

copper salt, $[C_6H_2(NO_2)_3O]_2[Cu(NH_3)_4(HO_2)_4]$, thin, golden leaflets; *cadmium* salt, $[C_6H_2(NO_2)_3O]_2[Cd(NH_3)_4(H_2O)_4]$, long, yellow needles; *zinc* salt, $[C_6H_2(NO_2)_3O]_2[Zn(NH_3)_4(H_2O)_4]$, small, egg-yellow needles; *silver* salt, $[C_6H_2(NO_2)_3O]_2[Ag(NH_3)_2]$, yellow needles or leaflets; the *barium* salt is more soluble than the silver compound; the magnesium, manganese, and calcium derivatives could not be obtained. A *cobalt* salt can, however, be prepared. Picrolonic acid gives very voluminous precipitates with cobaltiammines and gelatinous deposits with luteo- and purpureo-salts; the croceo-salt gives an amorphous precipitate after a short time.

The salts obtained by precipitation from aqueous solution with sodium *p*-dichlorobenzenesulphonate are tetrammine derivatives. The following are described: *nickel* salt, $C_{12}H_6O_6Cl_4S_2Ni,4NH_3,2H_2O$, pale violet powder, in which the two molecules of water can be replaced by ammonia by treatment with a current of the latter at 100°; *copper* salt, $C_{12}H_6O_6Cl_4S_2Cu,4NH_3,2H_2O$, small, dark blue prisms; *cadmium* salt, long, silky prisms; *zinc* salt, needles. H. W.

Acyl Derivatives of *p*-Aminophenyl Ethers. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.P. 332204; from *Chem. Zentr.*, 1921, ii, 648).—Acyl derivatives of *p*-aminophenol are treated with allyl haloids and an alkali. For example, p-*acetylaminophenyl allyl ether* prepared from *p*-acetylaminophenol, forms shining platelets, m. p. 94°. p-*Lactylaminophenyl allyl ether* is prepared from *p*-lactylaminophenol, and p-*formyl-aminophenyl*

allyl ether from *p*-formylaminophenol; it forms white platelets, m. p. 56°. G. W. R.

Aristol. G. H. WOOLLETT (*J. Amer. Chem. Soc.*, 1921, **43**, 553—561).—The products of the action of one, two, and four equivalents each of iodine and alkali hydroxide on thymol are respectively iodothymol, a gum almost completely soluble in alcohol, and aristol. Further, iodothymol is convertible into the others by treatment with suitable amounts of the reagents named. Ordinary aristol is a mixture of the gum (about 40%) with a faintly yellow product, insoluble in alcohol, mol. wt. 1940—2266, and resembling leuco-Lautemann's-Red in its oxidisability to a red product $(C_{10}H_{11}IO)n$, mol. wt. 3670—4430, sparingly soluble in alcohol. The colour of fresh aristol is due, not to adsorbed iodine, but to this product, which suffers gradual reduction and liberates iodine from the gummy portion. Lautemann's-Red similarly liberates iodine from iodothymol, of which an improved method of preparation is given. The dithymol formulæ for aristol (Bougault, *J. Pharm. Chim.*, 1918, [vii], 12, 221; Moles and Marquina, A., 1919, i, 270) are improbable, since all attempts to obtain dithymol from it by reduction have failed. J. K.

Urethanes of Thymol and Carvacrol. D. C. L. SHERK. (*Amer. J. Pharm.*, 1921, **93**, 207—222. Compare this vol., i, 239).—The sodium and potassium derivatives of nitrosothymol and nitrosocarvacrol were prepared by dissolving the nitrosophenol in the requisite quantity of 2*N*-alkali solution and evaporating the solution under reduced pressure; they decompose when heated, but are stable at temperatures up to 100°. The silver derivative of nitrosocarvacrol was obtained by adding silver nitrate solution to the oxime dissolved in alkali solution. The silver derivative of nitrosothymol was prepared in the same way. Benzoyl derivatives were made by the action of benzoyl chloride on alkali solutions of the nitrosophenols; the thymol *compound* had m. p. 105°, the carvacrol *compound* had m. p. 85—87°. The benzoyl derivative of carvacrol yields an oxime, but the benzoyl derivative of thymol is hydrolysed to the original nitrosothymol. W. P. S.

The Preparation of some Alkyl Derivatives of Resorcinol and the Relation of their Structure to Antiseptic Properties. TREAT B. JOHNSON and FREDERICK W. LANE (*J. Amer. Chem. Soc.*, 1921, **43**, 348—360).—The length, or weight, of the alkyl group introduced into the nucleus of resorcinol has a very marked influence in increasing the antiseptic value of resorcinol. The ethyl, *n*-propyl, and *n*-butyl derivatives are respectively 5, 14, and 26 times as strongly germicidal as resorcinol itself, the alkyl group being in each case in a position ortho to one hydroxyl group and para to the other.

In the preparation of resorcylaldehyde, the method of Dimroth and Zoeppritz (A., 1902, i, 293) requires modification in that the amount of alkali used for the hydrolysis of the Schiff base should be increased. Gattermann's process (A., 1908, i, 28), modified so that

gaseous hydrogen cyanide may be used, gave the best results. The methyl resorcinol obtained by reducing this aldehyde was apparently not pure, as its m. p. ranged from 70—104° according to the solvent used and the number of crystallisations (compare Clemmensen, A., 1914, i, 271, 418).

When zinc chloride is dissolved in *n*-butyric acid and the solution warmed with resorcinol, 2 : 4-*dihydroxyphenyl propyl ketone*, $C_3H_7\cdot CO\cdot C_6H_3(OH)_2$, m. p. 69—70°, is obtained, giving an *oxime* m. p. 189—190°. On reduction, the ketone yields 2 : 4-*dihydroxy-1-butylbenzene*, b. p. 155—175°/7 mm. W. G.

Preparation of *N*-Acylalkylhomopiperonylamines. E. MERCK (D.R.P. 332474; from *Chem. Zentr.*, 1921, ii, 648—649).—The potassium compound of formylhomopiperonylamine in toluene solution gives with methyl iodide a quantitative yield of *formyl methylhomopiperonylamine*, a thick strongly refracting oil, b. p. 194°/6 mm. G. W. R.

New Benzyl Esters Possessing an Anti-spasmodic Action. N. A. SHONLE and P. Q. ROW (*J. Amer. Chem. Soc.*, 1921, **43**, 361—365).—Benzyl chloride readily reacts with the alkali salts of the higher fatty acids, when they are dissolved in an excess of the hot fatty acid to give the benzyl esters. The esters may also be prepared by the interaction of benzyl alcohol and the acid chloride. *Benzyl laurate*, b. p. 209—211°/12 mm.; m. p. 8·5°; D_{25}^{25} 0·9457; n^{24} 1·4812; *benzyl myristate*, m. p. 20·5°; b. p. 229—231°/11 mm.; D_{25}^{25} 0·9321; n^{24} 1·4803; *benzyl palmitate*, m. p. 36·0°; D_{25}^{38} 0·9136; n^{50} 1·4689; *benzyl stearate*, m. p. 45·8°; D_{25}^{50} 0·9075; n^{50} 1·4663; *benzyl oleate*, b. p. 237°/7 mm.; D_{25}^{25} 0·9330; n^{25} 1·4875; *benzyl lactate*, b. p. 128—130°/5—6 mm.; n^{25} 1·5252; *benzyl* p-*aminobenzoate*, giving a *hydrochloride*, m. p. 184°; *benzyl* m-*nitrobenzoate*, b. p. 308°/760 mm. and *benzyl* m-*aminobenzoate* and its *hydrochloride* were prepared. The benzyl esters of the higher fatty acids are tasteless and odourless, and have an anti-spasmodic action. They are more readily hydrolysed by lipase than are the benzyl esters of aromatic acids. W. G.

Preparation of a Compound of Chloral with a Phenol. OSCAR HINSBERG (D.R.P. 332678; from *Chem. Zentr.*, 1921, ii, 648).—*Tri-β-chloro-α-*p*-acetylaminophenoxyethyl alcohol*,

$$NHAc\cdot C_6H_4\cdot O\cdot CH(OH)\cdot CCl_3,$$

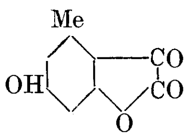
formed by the action of chloral on *p*-acetylaminophenol with or without a solvent, is a colourless, tasteless, crystalline powder, m. p. about 160°; which decomposes with frothing on sudden heating, giving chloral vapour, and also yields chloral when boiled with water. It is a more energetic soporific than chloral, from which it differs considerably in its effects on the organism. G. W. R.

Hydroxycarbinol Compounds. V. Products of the Action of Cyanogen and Hydrogen Chloride on Resorcinol and Orcinol. P. KARRER and J. FERLA (*Helv. Chim. Acta*, 1921, **4**, 203—212. Compare A., 1920, i, 441).—Cyanogen and hydrogen

chloride appear to act together as the dichlorodi-imide of oxalic acid, NH:CCl·CCl:NH, which should be capable of reacting with 1 mol. of resorcinol, giving the chloroimide, $C_6H_3(OH)_2$·C(NH)·CCl:NH, and with 2 mols. giving the imide, $C_6H_3(OH)_2$·C(NH)·C(NH)·$C_6H_3(OH)_2$, these products being hydrolysable respectively to resorcylglyoxylic acid and 2 : 4 : 2′ : 4′-tetrahydroxybenzil; the latter are, indeed, obtained in good yields, together with other compounds which prove incapable of purification or identification.

The action of cyanogen and hydrogen chloride on orcinol yields a yellow, crystalline precipitate, which consists principally of the compound $C_6H_3(OH)_2$·C(NH,HCl)·CCl:NH, and on hydrolysis yields orcylglyoxylic acid or its anhydride, but not the tetrahydroxy-diketone, $C_6H_2Me(OH)_2$·CO·CO·$C_6H_2Me(OH)_2$.

The interaction of resorcinol, cyanogen, and hydrogen chloride in absolute ethereal solution yields a yellow, crystalline precipitate, consisting principally of the hydrochlorides of the two compounds referred to above and of the compound $C_6H_3(OH)_2$·C(CN):NH,HCl, and yielding on hydrolysis: (1) A nitrogenous, chlorine-free compound, which forms hard, green crystals, m. p. 173°. (2) 2 : 4 : 2′: 4′-*tetrahydroxybenzil*, $C_6H_3(OH)_2$·CO·CO·$C_6H_3(OH)_2$, which crystallises in drusy aggregates of brownish-yellow crystals, m. p. 256° (? 263°) (decomp.), and forms a *diphenylhydrazone*, $C_{26}H_{22}O_4N_4$, m. p. 263° (decomp.) and a *tetramethyl ether*, $C_{18}H_{18}O_6$, forming thick, columnar crystals, m. p. 125—126°. (3) Resorcylglyoxylic acid, m. p. 168°, the m. p. 193° given by Bülow and Wagner (A., 1903, i, 647) being inaccurate; the *ammonium* and *silver* salts were analysed.



Orcylglyoxylic anhydride (annexed formulæ), m. p. 212°, is orange-yellow and in aqueous solution reddens Congo-blue paper.

Orcylglyoxylic acid dimethyl ether, $C_6H_2Me(OMe)_2$·CO·CO_2H [CO·CO_2H : Me : $(OMe)_2$ = 1 : 2 : 4 : 6,] small, white crystals, m. p. 138—139°, and gives a *methyl* ester, forming large, white crystals, m. p. 73—74°. Reduction of the acid ether by means of zinc dust and acetic acid yields, not dihydroxymethylmandelic acid, but orcinol. T. H. P.

The Reaction between Acid Haloids and Aldehydes. II. H. E. French and Roger Adams (*J. Amer. Chem. Soc.*, 1921, **43**, 651—659. Compare A., 1919, i, 20; this vol., i, 301).—This reaction is a very general one, occurring more readily and more completely with acid bromides than with the chlorides. It is also reversible, since the products, usually solid, gradually change, particularly in presence of zinc chloride, to a semi-solid mass very similar to the original product of reaction. The presence of halogen atoms or nitro-groups in either of the reactants retards the reaction but increases the stability of the products, whilst methyl and methoxyl groups have the opposite effect. The tendency to dissociation into their components explains the reaction of these compounds with water, already described, alcohol (giving ester, aldehyde, and hydrobromic acid), and dry ammonia (acid amide, aldehyde, and ammonium

haloid being produced). The reactions with primary aromatic and aliphatic amines are typified by the equations: $C_6H_5\cdot CO_2\cdot CHPhBr + NH_2Ph = CHPhBr\cdot NHPh + C_6H_5\cdot CO_2H$; $C_6H_5\cdot CO_2\cdot CHPhBr + 3NH_2Me = C_6H_5\cdot CO\cdot NHMe + NH_3MeBr + CHPh\colon NMe + H_2O$. Secondary aliphatic amines resemble ammonia in their action, whilst tertiary bases form additive compounds. Those with pyridine are crystalline and so are utilised to demonstrate that reaction has occurred in those cases in which the products are oils; they were also obtained by the addition of aldehyde to a mixture of acid haloid and pyridine. Dibenzoylhydrobenzoin is produced by the action of zinc dust or copper powders on phenylchloromethyl benzoate. Potassium cyanide and hydroxide cause complete hydrolysis. *Dibenzoyl*-pp-*dibromohydrobenzoin*, $C_{12}H_8Br_2(CH\cdot OBz)_2$, melts at 225°.

Condensation products (m. p. within brackets, where determined) are described of the following with benzaldehyde: *m*-nitrobenzoyl bromide (94—96°), *p*-nitrobenzoyl bromide (139—140°), 3 : 5-dinitrobenzoyl bromide (126—127°), *o*-chlorobenzoyl bromide (62—63°), *p*-chlorobenzoyl bromide (110—111°), *p*-bromobenzoyl bromide (119—121°), *o*-bromobenzoyl bromide (80°), *p*-iodobenzoyl bromide (123—124°), *m*-chlorobenzoyl bromide, anisyl bromide, *o*-toluoyl bromide, *m*-toluoyl bromide, 3 : 5-dinitrobenzoyl chloride (135—136°), cinnamoyl chloride (80°). With *o*-bromobenzaldehyde: *p*-nitrobenzoyl bromide (140—142°), 3 : 5-dinitrobenzoyl bromide (119—122°), *p*-bromobenzoyl bromide (154—156°). With *p*-bromobenzaldehyde: *p*-nitrobenzoyl bromide (146°), 3 : 5-dinitrobenzoyl bromide (151—152°), *o*-bromobenzoyl bromide (102—103°), *p*-bromobenzoyl bromide (120—121°), benzoyl chloride (109—110°), 3 : 5-dinitrobenzoyl chloride (145—146°), *p*-bromobenzoyl chloride (124—125°), cinnamoyl chloride (92—93°). With cinnamaldehyde: *m*-nitrobenzoyl bromide. With anisaldehyde: *p*-bromobenzoyl bromide, cinnamoyl chloride. With piperonaldehyde: cinnamoyl chloride. With methylvanillin: cinnamoyl chloride.

Condensation products were prepared from pyridine and phenylbromomethyl benzoate, $C_5H_3NBr\cdot CHPh\cdot OBz$, m. p. 180° (decomp.); phenylchloromethyl benzoate, $C_{19}H_{16}O_2NCl$, m. p. 192° (decomp.); *p*-methoxyphenylbromomethyl *p*-nitrobenzoate, $C_{20}H_{17}O_5N_2Br$, m. p. 126—128°; phenylbromomethyl *o*-toluate, $C_{20}H_{18}O_2NBr$, m. p. 206° (decomp.). J. K.

Derivatives of Anæsthesin [Ethyl *p*-Aminobenzoate]. H. Thoms and Kurt Ritsert (*Ber. Deut. pharm. Ges.*, 1921, **31**, 65—75).—The undermentioned derivatives of ethyl *p*-aminobenzoate, in which the hydrogen atom of the amino-group is replaced by various positive and negative groups, were prepared with the object of determining the effect of such substitution on the anæsthetic properties of the ester. In general the physiological action was much reduced by the substitution of amino-hydrogen atoms, and entirely disappeared with the introduction of negative groups. Only in the case of *p*-hydrazinobenzoic acid, where a second amino-group is substituted for a hydrogen atom, was the anæsthetic

action at all comparable with that of anæsthesin itself. The following derivatives are described: *ethyl* p-*N-allylthiocarbamidobenzoate*, prepared by the action of allylthiocarbamide on anæsthesine, forms colourless needles, m. p. 92°, and is but a feeble anæsthetic. *Ethyl* p-*N-allylcarbamidobenzoate*, prepared by the action of mercuric oxide on the preceding compound, forms colourless leaflets, m. p. 120°, and likewise has only a very slight anæsthetic action. *Ethyl* p-βγ-*dibromopropylthiocarbamidobenzoate*,

$$CO_2Et \cdot C_6H_4 \cdot NH \cdot CS \cdot NH \cdot CH_2 \cdot CHBr \cdot CH_2Br,$$

obtained by the action of bromine in chloroform solution on the allyl derivative, forms white needles, m. p. 146·5°, and has no anæsthetic action. *Ethyl* p-βγ-*dibromopropylcarbamidobenzoate*, similarly prepared from the allyl derivative, crystallises in needles, m. p. 146°, and is not an anæsthetic. *Ethyl* p-*hydrazinobenzoate*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot NH_2$, prepared by the reduction of diazotised anæsthesin, forms white leaflets, m. p. 114°, somewhat soluble in warm water, and gives a soluble *hydrochloride*, m. p. 214° (with decomp.). Both substances are good anæsthetics. The hydrazine readily condenses with aldehydes, ketones, etc., and the following condensation products are described. *Ethyl* p-iso-*propylidenehydrazinobenzoate*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot N{:}CMe_2$, m. p. 112°, *ethyl* p-*benzylidenehydrazinobenzoate*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot N{:}CHPh$, m. p. 160°. *Ethyl* p-*cinnamylidenehydrazinobenzoate*,

$$CO_2Et \cdot C_6H_4 \cdot NH \cdot N{:}CH \cdot CH{:}CHPh,$$

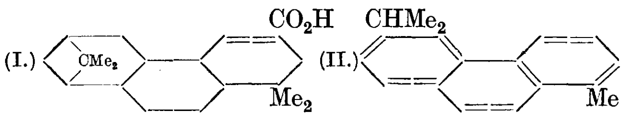
m. p. 156·5°. *Ethyl glucosazone*-pp-*dibenzoate*, m. p. 198°, *ethyl acetoacetate*-p-*carbethoxyphenylhydrazone*, yellow needles, m. p. 107°, which on heating at 130—140° are converted into *ethyl* 4-*methylpyrazolone*-1-*benzoate*, colourless needles, m. p. 145°. None of the above hydrazine derivatives have any anæsthetic action whatever. *Ethyl* p-*urethanobenzoate*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot CO_2Et$, was obtained by the action of ethyl chloroformate on anæsthesin, and formed colourless needles, m. p. 130·5°, with a feeble anæsthetic action. p-*Carbethoxyphenylaminoacetic acid*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H$, prepared by the action of monochloroacetic acid on anæsthesin, formed glistening leaflets, m. p. 163°, and *ethyl* p-*nitrobenzoyl*-p-*aminobenzoate*, $CO_2Et \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, from anæsthesin and *p*-nitrobenzoyl chloride, yellowish-white, rhombic crystals, m. p. 211°. Neither of these negatively substituted anæsthesins had anæsthetic properties. G. F. M.

Tolunaphthol [β-Naphthyl *p*-Toluate]. G. J. ÖSTLING (*Zeit. finn. Apoth.*, 1918; from *Chem. Zentr.*, 1921, i, 620).—β-*Naphthyl*-p-*toluate*, prepared from *p*-toluic acid and β-naphthol, is a white powder, m. p. 137° (from alcohol).

Unlike β-naphthyl benzoate, it is not resolved into its components by the action of pancreas infusion. G. W. R.

Constitution of the Resin Acids of Colophony. AD. GRÜN (*Zeit. Deut. Öl. Felt-ind.*, 1921, **41**, 49—52; from *Chem. Zentr.*, 1921, i, 496).—Previous investigations (Grün and Janko, *Chem. Umschau*, **26**, 35) have led to the conclusion that abietic acid,

like pinene, contains one double bond and a bridged linking instead of two double bonds. On the basis of further theoretical considerations, the constitution (I) is proposed for abietic acid, which explains its general behaviour better than any of the previous formulæ and also accounts for its formation from pinene.



This occurs by the condensation of a molecule of α- with one of β-pinene, an atom of hydrogen in each molecule wandering in such a manner as to form a hydrocarbon, $C_{20}H_{32}$, which is transformed into the acid (I) by the oxidation of a methyl to a carboxyl group. The behaviour of abietic acid when esterified or treated with halogens is readily explained on the basis of this formula. If such a compound is decarboxylated and dehydrated, preferably by being heated with acids, the carboxyl and a methyl group may be simultaneously eliminated in such a manner as to give a hydrocarbon, $C_{18}H_{18}$ (II), which is structurally isomeric with retene. Thermal decomposition of abietic acid yields small amounts of retene, which are probably obtained by isomerisation of this hydrocarbon. The formula is to be regarded as an example; other acids may be considered to be formed by the addition of pinene molecules in a different manner, thus leading to a number of abietic and pimaric acids. It is possible that some of them are derived from camphene or fenchene. H. W.

Action of Phosphoric Oxide on Salicylic Acid. ALFONS LANGER (*Apoth-Zeit.*, 1921, **36**, 42; from *Chem. Zentr.*, 1921, i, 569).—When salicylmetaphosphoric acid is heated with phenol at 150°, salol-red, described by Zimmermann (*ibid.*, **36**, 17) as well as the similar hydroxyphenylhydroxydiphenylcarbinols, occur in greater amounts than .salol, which can be obtained pure by repeated treatment with hot sodium hydroxide solution. The dyes thus obtained dye wool directly. *Salol-red*, $C_{19}H_{16}O_4$, is a reddish-brown powder, m. p. 116—119°, soluble like phenolphthalein in alkalis. The *compound*, $C_{19}H_{14}O_5$, obtained with resorcinol is a metallic-looking powder, but crystallises in reddish-yellow spikelets from dilute alcohol, m. p. 209°. The *compound*, $C_{38}H_{30}O_{15},3H_2O$, from pyrogallol forms reddish-violet platelets, m. p. 145°. The derivative prepared with aniline (two molecules), gives in glacial acetic acid solution with potassium dichromate an acid-stable blue dye insoluble in water and alkalis. The sodium salt of the sulphonic acid is soluble in water and dilute alcohol.

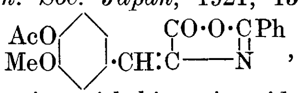
G. W. R.

5-Nitro-6-hydroxy-*m*-toluic Acid. K. PFISTER (*J. Amer. Chem. Soc.*, 1921, **43**, 375—376).—The substance described under this name by Mahon (A., 1882, 1205) obtained by nitrating 6-hydroxy-*m*-toluic acid at a high temperature is really dinitro-*o*-cresol. *5-Nitro-6-hydroxy-*m*-toluic acid* is readily obtained by

conducting the nitration with mixed acids under the usual conditions. It crystallises from acetic acid in pale yellow needles, m. p. 240°, and gives a *methyl* ester, m. p. 103°, which on reduction gives *methyl* 5-*amino*-6-*hydroxy*-m-*toluate*, m. p. 141°. W. G.

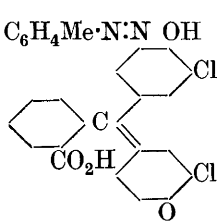
Spectro-chemistry of *cyclo*Butane Derivatives. G. J. ÖSTLING (*Finska Kemistzemfundets Medd.*, 1916; from *Chem. Zentr.*, i, 619).—Three *cyclo*butane derivatives were examined spectrographically. *Methyl pinate*, $C_{11}H_{18}O_4$, b. p. 125·4—126·2°/11 mm., $D_4^{14.3}$ 1·0560, does not decolorise potassium permanganate in alkaline solution. *Ethyl pinate*, $C_{13}H_{20}O_4$, b. p. 136—136·5°/7 mm., $D_4^{14.4}$ 1·0174; *methyl nopate*, $C_{11}H_{18}O_3$, b. p. 136°/13 mm., $D_4^{14.2}$ 1·0875; decolorises potassium permanganate slowly. The refractive indices for the three compounds were found, using different wave-lengths. G. W. R.

Preparation of 3 : 4-Dihydroxyphenylalanine. YOSHIO SUGII (*J. Pharm. Soc. Japan*, 1921, 130—136).—Vanillin gives the azlactone,



yellow needles, m. p. 185°, by condensation with hippuric acid in the presence of acetic anhydride and sodium acetate; this is converted into α-benzoylamino-*p*-hydroxy-*m*-methoxycinnamic acid, white prisms, m. p. 205°, by dissolving in 1% sodium hydroxide and then acidifying with 5% sulphuric acid. By reduction with 2% sodium amalgam in 10% sodium hydroxide solution and saturation with carbon dioxide, the acid gives α-benzoylamino-*p*-hydroxy-*m*-methoxyphenylpropionic acid, white leaflets, m. p. 157°, which is changed to 3 : 4-dihydroxyphenylalanine by heating with 20% hydrochloric acid at 150° for eight hours in a sealed tube. Protocatechualdehyde easily condenses with hippuric acid, producing an azlactone, m. p. 130—131°, which does not, however, yield α-benzoylamino-3 : 4-dihydroxycinnamic acid, but resinous matter. K. K.

Constitution of Phenolphthalein. F. CONSONNO and C. APOSTOLO (*Gazzetta*, 1921, **51**, i, 60—64).—Oddo's results (A., 1913, i, 1110; 1914, i, 601) supported, but did not definitely demonstrate, the accuracy of von Baeyer's dihydroxylic benzenoid formula for phenolphthalein, since, if the latter possessed a quinonoid structure, its interaction with two molecules of a diazo-salt might result in the introduction of two azo-groups into one of the nuclei, with formation of a compound of the composition found by Oddo. The formation of such a bisazo-compound is, however, rendered impossible if, in place of phenolphthalein, its dichloro-derivative is treated with a diazo-salt such as *p*-tolyldiazonium chloride. Under these conditions there results a monoazo-derivative to which a quinonoid structure may be attributed.



Dichlorophenolphthalein, prepared by condensation of phthalic anhydride with *o*-chlorophenol, is a straw-yellow compound, m. p. 98°.

p-*Tolylazodichlorophenolphthalein* (formula on p. i, 346) forms minute, brownish-yellow crystals, m. p. 158°. T. H. P.

Picrotoxin. X. Degradation of α-Picrotinic Acid, $C_{15}H_{20}O_8$, to the Acid, $C_{13}H_{14}O_4$. PAUL HORRMANN and MAX HAGENDORN (*Arch. Pharm.*, 1921, **259**, 7—15).—α-Picrotinic acid (Angelico, A., 1910, i, 404; Horrmann, A., 1913, i, 70) has been converted by Angelico (*loc. cit.*) by the action of boiling dilute sulphuric acid into picrotinketol, $C_{14}H_{16}O_4$, which is stated to be oxidised by permanganate to a monobasic acid having the same composition. Since, however, this is impossible, the authors have repeated the work and find that the product of oxidation is a crystalline monobasic acid, $C_{13}H_{14}O_4$, which appears to be contaminated with a small quantity of an unidentified dicarboxylic acid.

α-Picrotinic acid or its methyl ester is converted by boiling sulphuric acid (40%) into picrotinketol, a pale yellow, viscous liquid, which does not show any tendency to crystallise, b. p. 225—226°/10 mm., in 45% yield, considerable amounts of a substance which is sparingly soluble in ether and of distillation residue, m. p. about 130°, being obtained. The ketol yields an *oxime*, m. p. 206° (slight decomp.), a *semicarbazone*, decomp. 226°, an *acetate*, m. p. 84°, and a *phenylosazone*, $C_{14}H_{14}O_2(:N\cdot NHPh)_2$, pale yellow crystals, m. p. 204°. It is oxidised by potassium permanganate when suspended in sulphuric acid (25%) to at least two neutral *substances*, one of which, $C_{11}H_{12}O_2$, has m. p. 84°, and to a mixture of acids. The isolation of the acid, $C_{13}H_{14}O_4$, slender needles, m. p. 165°, from the latter is accomplished by the partial precipitation of the neutralised solution with silver nitrate, which causes the immediate separation of the silver salt of the adventitious acid; the filtrate from the precipitate slowly deposits the *salt*, $C_{13}H_{13}O_4Ag$, in colourless rosettes from which the pure acid is readily isolated. H. W.

Catalytic Hydrogenations by means of Copper. PAUL SABATIER and BENNOSUKE KUBOTA (*Compt. rend.*, 1921, **172**, 733—736).—Examples of the hydrogenation of certain aromatic aldehydes and ketones by means of copper are given. The catalyst is prepared by very slowly reducing tetracupric hydroxide at 200°. When benzaldehyde and hydrogen are passed over this catalyst at 350° the main reaction is $C_6H_5\cdot CHO + H_2 = C_6H_6 + CO + H_2$, together with a slight secondary reaction, $C_6H_5\cdot CHO + 2H_2 = C_6H_5Me + H_2O$. The carbon monoxide is not reduced to methane. Under similar conditions, acetophenone is slowly converted into ethylbenzene, and phenyl ethyl ketone gives propylbenzene. Benzoylpropanone is, however, decomposed, and the products are acetophenone, acetaldehyde, and ethyl alcohol, together with a little ethylbenzene and water as secondary products. Benzoquinone is hydrogenated at 300°, giving quinole. Phthalic anhydride, when hydrogenated, gives at first benzene and carbon monoxide, but

soon the reaction changes and phthalide is formed, there being an accessory change yielding toluene, carbon monoxide, and water.

W. G.

The Influence of Carbon Disulphide in the Friedel-Crafts' Synthesis. P. J. MONTAGNE (*Rec. trav. chim.*, 1921, **40**, 247—248).—In the preparation of 4-methoxybenzophenone, the action proceeds normally if 4-methoxybenzoyl chloride, benzene, and aluminium chloride are warmed together without any diluent, but if carbon disulphide is added as a diluent the product is a resinous mass with a nauseating odour from which it was possible to isolate but little 4-hydroxybenzophenone and 4-methoxybenzoic acid (compare Peterson, A., 1911, i, 879; Ullmann and Goldberg, A., 1902, i, 792).

W. G.

Salt-like Additive Products of the Carbon Double Bond with Acids. F. KEHRMANN and IWAN EFFRONT (*Ber.*, 1921, **54**, [*B*], 417—425).—The possibility that the free partial valencies of the carbon double bond may enable hydrocarbons to unite with acids to form salts has been advanced, but subsequently discarded by von Baeyer. The hypothesis is now revived by the authors to account for the formation of two series of salts by the triphenylmethane dyes (A., 1918, i, 311) and for the behaviour of certain unsaturated ketones towards acids. Thus, distyryl ketone gives mono- and di-acid salts which are lemon-yellow and orange-red in colour, and yield different absorption spectra, so that it is necessary to assume that combination can occur at one double bond in addition to that taking place at the oxygen atom. The optical behaviour of distyryl ketone in contact with strong acids cannot possibly be explained by the basic functions of oxygen alone, since experience has shown that an increase in the number of molecules of acid located at a single point of attachment has not a marked influence on the colour of the monacid salts. It appeared probable that the introduction of a greater number of double bonds into the molecule of distyryl ketone would increase the number of salts obtainable, and it is found that dicinnamylideneacetone gives at least three differently coloured additive products with concentrated sulphuric acid.

It has been shown previously that azobenzene has two points of attachment for acids $\left(\text{thus } \begin{array}{c} \mathrm{R{-}N \equiv\equiv N{-}R} \\ \diagup\diagdown \quad \diagup\diagdown \\ \mathrm{H \;\; Ac \;\; H \;\; Ac} \end{array}\right)$, one of which is suppressed when a sulphonic group is introduced into the benzene molecule, and similar suppression must be expected to take place even more readily with doubly-linked oxygen and with carbon. Comparison of oxygen and nitrogen compounds shows that an extensive analogy in functions and properties exists between OH and NH_2, O and NH, oxonium and ammonium, and, in particular, that the unsaturated oxonium and azonium groups $\left(\begin{array}{c} \mathrm{:C{=}O{-}C:} \\ | \\ \mathrm{Ac} \end{array} \text{ and } \begin{array}{c} \mathrm{:C{=}N{-}C:} \\ \diagup\diagdown \\ \mathrm{R \quad Ac} \end{array}\right)$ behave similarly. It may be regarded as established that the third and fourth valencies of

oxygen are more pronouncedly subsidiary in character than the fourth and fifth valencies of nitrogen, and that the difference is one of degree only and not of kind. Extending these observations to doubly-linked carbon, the authors are drawn to the conclusion that, under suitable conditions, it can also function with two subsidiary valencies which can cause the addition of acids with the formation of salts. A parallel is therefore drawn between bivalent oxygen, tervalent nitrogen, and quadrivalent carbon on the one hand and quadrivalent oxygen, quinquevalent nitrogen, and sexavalent carbon on the other. H. W.

The Formation and Properties of Dithio-ketones ($R_2C⁚S⁚S$) and Dithio-ethers ($R_2S⁚S$). I. KUVERJI GOSAI NAIK (T., 1921, **119**, 379—385.

Dibromoanthraquinones. M. BATTEGAY and J. CLAUDIN (*Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632—635).—There are ten possible dibromoanthraquinones, and that used by Graebe and Liebermann as the intermediate product in their classical synthesis of alizarin might be assumed to be the 1 : 2-derivative, but a study of various dibromoanthraquinones has shown that hypothesis to be incorrect.

1 : 2-*Dibromoanthraquinone*, obtained from 2-bromo-1-amino-anthraquinone, forms yellow crystals, m. p. 223°, dissolves in sulphuric acid with an orange-yellow colour, and on dilution separates in pale yellow flocks; it is readily converted into alizarin by the action of milk of lime at 200°.

1 : 3-*Dibromoanthraquinone*, obtained from 2 : 4-dibromo-1-amino- or 1 : 3-dibromo-2-aminoanthraquinone, forms orange-yellow crystals, m. p. 209—210°, dissolves in sulphuric acid with a yellow colour, and on dilution separates in yellow flocks; it may be transformed into purpuroxanthin.

1 : 4-*Dibromoanthraquinone*, obtained from 1 : 4-diaminoanthraquinone, forms orange needles, m. p. 196°, dissolves in sulphuric acid with a yellow colour, and on dilution separates in orange-yellow flocks. When 4-bromo-1-nitroanthraquinone is reduced, bromine is eliminated, and 1-aminoanthraquinone is formed.

2 : 3-*Dibromoanthraquinone*, obtained from 3-bromo-2-amino-anthraquinone, forms yellow needles, m. p. 281°, dissolves in sulphuric acid with an orange-yellow colour, and on dilution separates in almost white flocks. By the action of milk of lime at 200°, it is transformed into hystazarin, which is readily converted into alizarin by heating with sulphuric acid. When 2 : 3-dibromoanthraquinone is fused with sodium hydroxide, a reddish-violet solution reminiscent of sodium alizarinate is obtained, whilst hystazarin behaves in a similar manner and cannot be regenerated from the reddish-violet solution.

1 : 5-*Dibromoanthraquinone*, golden-yellow needles, m. p. 292°, and 1 : 8-*dibromoanthraquinone*, yellow crystals, m. p. 230°, which are obtained by the action of bromine on the corresponding anthraquinonedisulphonic acids, dissolve in sulphuric acid with an orange colour, and on dilution separate in white flocks.

2 : 7-*Dibromoanthraquinone*, obtained from 2 : 7-diaminoanthraquinone, forms yellow spangles, m. p. 248°, dissolves in sulphuric acid with an orange colour, and on dilution separates in white flocks.

The dibromoanthraquinone of Graebe and Liebermann is stated to be obtained by the direct bromination of anthraquinone at 100°, or by the oxidation of tetrabromoanthracene, but the two products are not identical. In the former case, the product is shown to be 2 : 7-dibromoanthraquinone, and, in the latter 2 : 3-dibromoanthraquinone. F. M. R.

Dinitroanthraquinones. M. Battegay and J. Claudin (*Bull. Soc. Ind. Mulhouse*, 1920, **86**, 628—631).—When the crude dinitration product of anthraquinone is reduced, the whole of the 1 : 5-, almost the whole of the 1 : 8-, and a large proportion of the 2 : 6-diaminoanthraquinone can be separated. The residue of diaminoanthraquinones has been examined by diazotisation and conversion into the corresponding dihydroxy-derivatives. The isomerides were separated, and the presence of 2 : 6-, 1 : 8-, 1 : 6-, 1 : 7-, and 2 : 7-dihydroxyanthraquinones established. Based on these results, it is calculated that the dinitration of anthraquinone gives rise to 37% 1 : 5-, 37% 1 : 8-, 4·2% 1 : 7-, 3·6% 1 : 6-, 6% 2 : 6-, and 4% 2 : 7-dinitroanthraquinone. The missing 8·2% must be attributed, at least in part, to losses during manipulation.

S. N. Dhar (T., 1920, **117**, 1001) claimed that 1 : 2-, 1 : 3-, 2 : 6-, and 1 : 5-dinitroanthraquinones are formed on dinitration, and identified these products by conversion into the corresponding dibromoanthraquinones. The authors have repeated Dhar's experiments and point out that the latter neglected entirely the product contained in the mother liquors of nitration, which may be precipitated by water, m. p. 200—220° (crude), and represents about 22% of the total yield. In order to reproduce the exact conditions, the authors also discarded this portion, and the crude nitration product, m. p. 315—320°, was brominated. The crude bromination product, m. p. 215—220°, extracted with alcohol, yielded a soluble portion, *A*, and an insoluble portion, *B*. *A* was separated by fractional crystallisation into a product, m. p. 260°, sparingly soluble in alcohol, and a product, m. p. 234°, more readily soluble in alcohol. Dhar regarded the former as 1 : 2- and the latter as 1 : 3-dibromoanthraquinone, but when these products are compared with 1 : 2- and 1 : 3-dibromoanthraquinone (cf. preceding abstract), it is clear that neither is a homonuclear dibromo-derivative. *B* is completely soluble in benzene, and is separated by fractional crystallisation into 1 : 5-dibromoanthraquinone, m. p. 292°, and 1 : 8-dibromoanthraquinone, m. p. 224°.

The formation of a dibromoanthraquinone, m. p. above 360°, insoluble in benzene was not observed. F. M. R.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. Badische Anilin- & Soda-Fabrik (D.R.P. 332013; from *Chem. Zentr.*, 1921, ii, 559—560. An addition to D.R.P. 329247 [this vol., i, 274]).—1-Arylaminoanthra-

quinones or their nuclear substitution products which contain reactive substituents in the ortho position to the amino-group are condensed with primary aromatic amines. 1-Anilino-2-methoxyanthraquinone (from 1-bromo-2-methoxyanthraquinone and aniline) gives with aniline and potassium hydroxide a condensation product identical with that described in the main patent. The same substance is prepared from 1-chloro-2′-anilinoanthraquinone (from 1-chloroanthraquinone and *o*-chloroaniline). H. W.

Phototropism in Solution. I. BAWA KARTAR SINGH (*J. Amer. Chem. Soc.*, 1921, **43**, 333—334).—A solution of α-naphthylaminocamphor in chloroform is colourless in the dark, but on exposure to direct sunlight becomes green within one minute. Similar changes are noted with chloroform solutions of *m*-phenylenebisaminocamphor or *ar*-tetrahydro-α-naphthylaminocamphor. In every case the green colour completely vanishes when the green solutions are placed in the dark for about twenty-four hours. The time required for transformation from colourless to coloured varies with the intensity of the illumination. These facts are not in accord with the theory of Senier and Shepheard (T., 1909, **95**, 1944) as to phototropic transformation. In the above three cases, the changes may possibly be of the keto-enol type, as the corresponding imino-derivatives do not show this phototropism. W. G.

Essential Oil of *Juniperus taxifolia*. YEINOSUKA SHINOSAKI (*J. Chem. Ind. Japan*, 1921, **24**, 202—208).—The oil was obtained by distillation of the leaves and twigs of *Juniperus taxifolia*, a coniferous plant indigenous to the Ogasawara Islands. The yield was 0·24% of a light green oil. The chief constituents of the oil were mainly α-pinene (above 50% mainly *l*-α-pinene containing a small quantity of *r*-α-isomeride) and perhaps a bicyclic terpene, an uncombined alcohol ($C_{10}H_{18}O$), an ester, a sesquiterpene, and a sesquiterpene alcohol. K. K.

Essential Oil of *Vitex trifolia*. YEINOSUKA SHINOSAKI (*J. Chem. Ind. Japan*, 1921, **24**, 191—202).—The oil is obtained by the distillation of the leaves and twigs of *Vitex trifolia*, L. (perhaps *Vitex ovata*, Mak.), grown in the Ogasawara Islands and the Kanagawa Prefecture, yield 0·11—0·28%; it has a brown colour and a characteristic odour. The chief constituents of the oil are *l*-α-pinene, which does not give a solid nitrosochloride, and camphene (together 55%); terpinyl acetate (10%), b. p. 84—86°/15 mm., D^{15} 0·9629, n_D^{20} 1·4670, diterpene alcohol ($C_{20}H_{32}O$ or $C_{20}H_{34}O$) (20%), b. p. 165—167°/4 mm., D^{15} 0·9760, n_D^{20} 1·5143, $[\alpha]_D$ + 46° 39′, and saponification number after acetylation, 42·02. K. K.

Siam Benzoin. II. Siaresionolic Acid. FRIEDRICH REINITZER (*Arch. Pharm.*, 1921, **259**, 1—6. Compare A., 1915, i, 431).—*d*-Siaresinolic acid, the investigation of which has been carried out by Zinke and Lieb (A., 1918, i, 398; 1919, i, 128) at the author's request, is most conveniently prepared by treating the crude benzoin with warm aqueous sodium hydroxide (4—5%)

when sodium *d*-siaresinolate remains as a very sparingly soluble precipitate which can be readily purified by crystallisation from alcohol. The free acid has $[\alpha]_D^{25\cdot6} + 37\cdot793$ in ethyl alcoholic solution (96%), m. p. 260° (Zinke and Lieb give 274—275°). The additive compound of *d*-siaresinolic acid and acetic acid,

$$C_{30}H_{48}O_4,C_2H_4O_2,$$

forms rhombic crystals which suddenly lose acetic acid when heated to 174° and leave *d*-siaresinolic acid, m. p. 279°. The latter does not contain a methoxy-group. It does not play a part in the gradual discoloration suffered by the resin when preserved. *Potassium* d-*siaresinolate* crystallises in needles which dissolve freely in water and alcohol.

Zinke and Lieb have described the oxidation of *d*-siaresinolic acid by chromic and glacial acetic acids to a strongly lævorotatory, crystalline acid, $C_{27}H_{40}O_4$, for which the author proposes the name l-*prabangic acid* (derived from the Luang-Prabang region, from which the bulk of the resin is obtained). H. W.

Siam Benzoin. III. Properties and Constitution of Lubanol Benzoate. FRIEDRICH REINITZER (*Arch. Pharm.*, 1921, **259**, 60—69).—Lubanol benzoate (compare A., 1915, i, 431), $C_{17}H_{16}O_4$, crystallises in plates, m. p. 72·8°, and contains one methoxy-group. It readily becomes oxidised when exposed to warm air, and then exhibits a series of colour changes which are precisely analogous to those shown by the crude resin. It readily loses benzoic acid when heated at 120—140°, and on further rise of temperature evolves the odour of oil of carnations and subsequently of guaiacol. It is optically inactive. A lengthy series of colour reactions is given. The benzoate is very readily hydrolysed either in acid or alkaline solution, but the isolation of lubanol in the pure condition has been impossible up to the present on account of the great susceptibility of the substance, particularly in alkaline solution, to further change. The isolation and analysis of a dibenzoate and a dibromobenzoate (compare Zinke, this vol., i, 187) lead the author to the conclusion that lubanol is identical with coniferyl alcohol, or is closely related to this substance; the point cannot, however, be definitely decided until a crystalline specimen of lubanol has been obtained, but the colour reactions of the benzoate are in complete harmony with this conception. H. W.

Solubility of Crystalline Substances in Caoutchouc. G. BRUNI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 75—80; also *Giorn. Chim. Ind. Appl.*, 1921, **3**, 51—53).—Towards various solvents caoutchouc behaves rather as solvent than as solute. Admixture of 10% of azobenzene with caoutchouc yields a transparent, orange-yellow jelly, which rapidly becomes opaque owing to deposition of crystalline azobenzene. Thermal analysis of the binary systems formed by resin-free caoutchouc with azobenzene, naphthalene, and *p*-toluidine shows that these systems exhibit normal behaviour; the caoutchouc acts towards the crystalline constituent as an ordinary solvent, forming true, saturated solutions, which readily exhibit supercooling and supersaturation. The colloidal character

of caoutchouc plays no part in these phenomena. The marked concavity towards the concentration axis of the curves connecting temperature and composition indicates the formation of complexes between the caoutchouc and the crystalline components of the systems. Prolonged heating of the systems produces no permanent alteration in the molecular state of the caoutchouc, which behaves quite normally when subsequently separated from the crystalline compounds. T. H. P.

The Extraction of Tannin (Gallotannic Acid). E. KNAPE (*Chem. Zeit.*, 1921, **45**, 239—241).—Galls are swollen with water, ground up and extracted with ethyl ether or ether–alcohol mixture for twenty to thirty minutes in a cylindrical shaker fitted with tubes. The extract is filtered off, and three more extractions are made. A clearer, brighter solution of gallotannic acid is obtained in this way than from dry powdered galls, and less solvent is required. The ether can be replaced by trichloroethylene or dichloroethylene with equally good results. D. W.

4 : 7-Dihydroxycoumarin. K. HUGO BAUER and FELIX SCHODER (*Arch. Pharm.*, 1921, **259**, 53—59).—The experiments were undertaken with the object of examining the applicability of Hösch's reaction (A., 1915, i, 820) to the esters of cyano-fatty acids. It is found that resorcinol condenses with ethyl cyanoacetate in the expected manner, but that the ketimine of ethyl dihydroxybenzoylacetate cannot be isolated as such owing to the facility with which it is hydrolysed to the corresponding acid, which immediately loses water with the formation of 4-*imino*-7-*hydroxycoumarin*, $OH\cdot C_6H_3<\begin{matrix} C(NH)\cdot CH_2 \\ O\text{———}CO \end{matrix}$, from which 4 : 7-*dihydroxycoumarin* is readily prepared.

A solution of resorcinol and ethyl cyanoacetate in dry ether is treated with zinc chloride and dry hydrogen chloride and allowed to remain at the ordinary temperature for seven or eight days, when 4-imino-7-hydroxycoumarin separates as a pale red, microcrystalline powder, m. p. 311° (decomp.) after darkening at 309°. It is converted by boiling sodium hydroxide solution into 4 : 7-dihydroxycoumarin, colourless, matted needles, m. p. 264° (decomp.) after becoming brown at 260°, the constitution of which is deduced from its conversion by potassium hydroxide into 2 : 4-dihydroxyacetophenone, m. p. 143°. 4 : 7-Dihydroxycoumarin is transformed by diazomethane or methyl sulphate into 4 : 7-*dimethoxycoumarin*, small, colourless needles, m. p. 162°, and by acetic anhydride and sodium acetate into 4 : 7-*diacetoxycoumarin*, prisms, m. p. 145·5°. 4-*Anilino*-7-*hydroxycoumarin*, $OH\cdot C_6H_3<\begin{matrix} C(NPh):CH \\ O\text{———}CO \end{matrix}$, crystallises in pale brown needles, m. p. 176°. Concentrated sulphuric acid and nitric acid (D 1·4) transform 4 : 7-dihydroxycoumarin into 6 : 8(?)-*dinitro*-4 : 7-*dihydroxycoumarin*, pale yellow needles, which become brown at 190° and blacken, without melting, between 240° and 270°. Bromine in carbon tetrachloride solution gives 8(?)-*bromo*-

4 : 7-*dihydroxycoumarin*, shining, pale yellow leaflets, m. p. 127°. Reduction of 4 : 7-dihydroxycoumarin by zinc dust and glacial acetic acid or by zinc and hydrogen chloride in the presence of alcohol leads to the formation of 7-*hydroxydihydrocoumarin*, almost colourless needles, m. p. 252° (decomp.) after darkening above 210°.

In the preparation of 4-imino-7-hydroxycoumarin from equimolecular quantities of ethyl cyanoacetate and resorcinol, practically half of the latter is recovered unchanged. An experiment in which two molecular proportions of the ester were employed yielded a product which was converted by sodium hydroxide into the *substance*, $C_{12}H_6O_6$; apparently two coumarin rings have been formed, one from each hydroxy-group, and the substance may be formulated,

$$\begin{matrix} CH{:}C(OH) \\ | \qquad\qquad \\ CO\text{———}O \end{matrix}\!>\!C_6H_2\!<\!\begin{matrix} C(OH){:}CH \\ \qquad\qquad | \\ O\text{———}CO \end{matrix}.$$

H. W.

Preparation of Compounds of the Morphine Alkaloids with Derivatives of Barbituric Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.P. 330814; from *Chem. Zentr.*, 1921, ii, 604. Compare A., 1920, i, 756. An addition to D.R.P. 322335, A., 1920, i, 756).—In extension of the main patent, the similar condensation of the alkaloids of the morphine group or their derivatives with arylalkylbarbituric acids is now claimed. The following examples are cited: *morphine-phenylethylbarbituric acid*, needles, m. p. 250°; *ethylmorphine-phenylethylbarbituric acid*, from the components in boiling benzene, needles, m. p. 87°; *codeine-phenylethylbarbituric acid*, from the components in boiling absolute alcohol, crystals, m. p. 80°. The substances are suitable as soporifics.

H. W.

An Alkaloid from *Sinomenium diversifolius*. NISABURÔ ISHIWARI (*Chûgai Iji Shimpô*, 1920, No. **959**, 1—20).—A new alkaloid, *sinomenine*, $C_{16}H_{19}NO_3,H_2O$, white needles, m. p. 161°, was isolated from the hot alcoholic extract of *Sinomenium diversifolius* (*Miq.*). The *hydrochloride* forms white prisms, m. p. 224°, and the *picrate*, yellow plates, m. p. about 140°. Its physiological action resembles that of quinine. K. K.

The Action of Alkyl Nitrates on Piperidine. DAVID TEMPLETON GIBSON and ALEXANDER KILLEN MACBETH (T., 1921, **119**, 438—442).

The Hydrates of Pyridine. H. PARISELLE (*Compt. rend.*, 1921, **172**, 673—676).—Although there is marked development of heat when pyridine and water are mixed, the author is of the opinion that the hydrates of pyridine as described in the literature do not exist as stable substances. W. G.

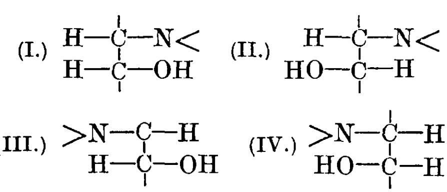
Preparation of Pyridine Bases. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 147000. An addition to 146869; see A., 1921, i, 52).—A considerable improvement in the yield of pyridine bases and an acceleration of the reaction is realised by heating paracetaldehyde with aqueous ammonia in presence of an ammonium salt such as the chloride or acetate. For example, a 70% yield of 2-methyl-5-ethylpyridine is obtained by heating for

eight hours at 180° a mixture of 120 parts of paracetaldehyde, 230 parts of 5·5% aqueous ammonia, and 20 parts of ammonium chloride. G. F. M.

Preparations of Alcohols and Amino-alcohols of the Quinoline Series. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.P. 330813; from *Chem. Zentr.*, 1921, ii, 603).—Quinolylketones or quinolylaminoketones are reduced in alcoholic solution in the presence of alkali alkoxide by metals, such as zinc or aluminium, the hydroxides of which have feebly acidic properties, enabling them to form salts with strong bases. The quinoline nucleus and the unsaturated side chain are not affected by this treatment, which exclusively reduces the carbonyl to the secondary alcoholic group. The process marks a decided advance towards the synthesis of quinine and its derivatives. Quininone,

$$OMe{\cdot}C_9H_5N{\cdot}CO{\cdot}C_9H_{14}N,$$

is converted by powdered aluminium, alcohol, and sodium ethoxide into a mixture of secondary alcohols from which pure quinine, $OMe{\cdot}C_9H_5N{\cdot}CH(OH){\cdot}C_9H_{14}N$, m. p. 177°, $[\alpha]_D^{14}$ + 158·7° in absolute alcoholic solution, is separated through the sparingly soluble normal sulphate; quinidine, m. p. 171·5°, $[\alpha]_D^{14}$ + 249·7° in alcohol, is isolated by making the mother liquors alkaline, and extracting with ether. Dihydrocinchoninone, $C_9H_6N{\cdot}CO{\cdot}C_9H_{16}N$, when treated with zinc dust or powdered aluminium, gives dihydrocinchonine, dihydrocinchonidine, and the two further theoretically possible stereoisomeric *alcohols* corresponding with the annexed formulæ. The two former substances show complete agreement in melting point and specific rotation with the minor cinchona alkaloids. Neither the third nor the fourth isomeride has yet been isolated from natural sources: the one has m. p. 126°, $[\alpha]_D^{14}$ + 88·5° and the other m. p. 106° and $[\alpha]_D^{18}$ + 48° in absolute alcoholic solution. The two new compounds are transformed by boiling dilute acetic acid into dihydrocinchotoxine, which passes through a bromo-imine into dihydrocinchoninone, m. p. 138°. Evaporation of an ethereal solution of the product of reduction of cinchotoxine,



$$C_9H_6N{\cdot}CO{\cdot}[CH_2]_2{\cdot}C_7H_{12}N,$$

gives *cinchotoxol*, a pale yellow, viscous oil which becomes partly solid when rubbed; the reactions for quinatoxines with diazobenzenesulphonic acid or with nitrobenzene containing nitrothiophen give negative results. 6-Methoxy-4-quinolyl methyl ketone, $OMe{\cdot}C_9H_5N{\cdot}COMe$, is converted when boiled with alcohol, sodium ethoxide, and aluminium powder into *6-methoxy-4-quinolylmethylcarbinol*, m. p. 120—121°. 6-Methoxy-4-quinolylpiperidinomethylcarbinol, needles, m. p. 109°, is prepared from the corresponding ketone; it is identical with the product described by Rabe, Pasternak, and Kindler (A., 1917, i, 284). H. W.

The System: Picric Acid–5–Phenylacridine. HENRY BASSETT and THOMAS ARTHUR SIMMONS (T., 1921, **119**, 416—417).

New Nitrogenous Peroxide Compounds from Formaldehyde. C. VON GIRSEWALD and H. SIEGENS (*Ber.*, 1921, **54**, [*B*], 492—498).—Further investigation of the action of nitrogenous bases on formaldehyde and hydrogen peroxide indicates that the mechanism can be expressed by the general scheme, $RN{<}{H \atop H} + {HO{\cdot}CH_2{\cdot}O \atop HO{\cdot}CH_2{\cdot}O} = 2H_2O + RN{<}{CH_2{\cdot}O \atop CH_2{\cdot}O}$. The formulæ $ {O{\cdot}CH_2 \atop O{\cdot}CH_2}{>}N{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}N{<}{CH_2{\cdot}O \atop CH_2{\cdot}O}$ and $H_2N{\cdot}CO{\cdot}N{<}{CH_2{\cdot}O \atop CH_2{\cdot}O}$ are therefore now assigned to hexamethylenetriperoxidediamine (Baeyer and Villiger, A., 1900, i, 626; von Girsewald, A., 1912, i, 834) and dimethyleneperoxidecarbamide (tetramethylenedicarbamide diperoxide, von Girsewald and Siegens, A., 1915, i, 387).

Trimethyleneperoxideazine [4-*Methyleneamino*-3 : 5-*dihydro*-1 : 2 : 4-*dioxazole*], $CH_2{:}N{\cdot}N{<}{CH_2{\cdot}O \atop CH_2{\cdot}O}$, is prepared under certain conditions which are fully described in the original from formaldehyde, hydrazine sulphate, and hydrogen peroxide in aqueous solution; when dissolved in nitric acid, it gives a very unstable *compound* when treated with silver nitrate, and the *substance*,

$$(CH_2{:}N_2{:}CH_2)_3,2HgCl_2,$$

with mercuric chloride. Similarly, ethylamine yields *dimethyleneperoxide-ethylamine* [4-*ethyl*-3 : 5-*dihydro*-1 : 2 : 4-*dioxazole*], $EtN{<}{CH_2{\cdot}O \atop CH_2{\cdot}O}$, a colourless, viscous, neutral, unstable liquid. The new five-membered ring is more or less readily hydrolysed by acids, giving formaldehyde, hydrogen peroxide, and ammonia or its derivatives. The peroxides are generally almost insoluble in water and the usual organic media. Their high oxidising power is only exhibited after hydrolysis. They are more or less explosive, the property being most marked in the case of hexamethylenetriperoxidediamine. Their stability appears to depend on the strength of the nitrogenous base, increasing with increase of the latter. H. W.

Di- and Tri-phenylmethane Series. I. *p*-Alkylaminobenzophenones. JAKOB MEISENHEIMER, EUGEN VON BUDKEWICZ, and GEORG KANANOW (*Annalen*, 1921, **423**, 75—94).—The authors confirm Hess's statement (A., 1885, 783) that the product of the interaction of benzoyl chloride and dimethylaniline is benzomethylanilide, NMePhBz, and not dimethylaminodibenzoylbenzene, as asserted by Michler and Dupertius (A., 1877, ii, 333).

Repetition of Fischer's work (A., 1877, ii, 606; 1881, ii, 587) shows that no dimethylaminobenzophenone, m. p. 38—39°, exists (compare Neundlinger, A., 1915, i, 954); the same holds for Fischer's dinitrodimethylaminobenzophenone, m. p. 142°. Further, the action of benzoic acid on dimethyl-*o*-toluidine in presence of phosphoric oxide gives, not 4-dimethylamino-3-methylbenzophenone (Fischer, *loc. cit.*), but benzomethyl-*o*-toluidide, $C_6H_4Me{\cdot}NMeBz$,

which may also be synthesised from methyl-*o*-toluidine and benzoyl chloride.

A good general method for the preparation of unsymmetrical aminobenzophenones consists in heating together an anilide, a tertiary amine, and phosphoryl chloride, the imino- or amino-chloride thus formed condensing with the tertiary amine to the auramine-like dimethylaminobenzophenoneanil, which decomposes into aniline and *p*-dimethylaminobenzophenone when heated with a dilute mineral acid:

$$NHPhBz \longrightarrow NPh{:}CPhCl \longrightarrow NPh{:}CPh{\cdot}C_6H_4{\cdot}NMe_2.$$

In this way dimethylamino-, diethylamino-, and dimethyldiethyldiamino-benzophenones have been obtained pure and in good yields.

The method does not, however, serve for the preparation of 4 : 4′-tetramethyldiamino-3-methylbenzophenone from *p*-dimethylaminobenzanilide and dimethyl-*o*-toluidine. The slight reactivity of the dimethyl-*o*-toluidine prevents the reaction at a low temperature, whereas, if the tertiary base is heated with dimethylaminobenzanilide or benzanilide and phosphoryl chloride at 80°, the imino-chloride is formed but does not react with the dimethyl-*o*-toluidine. At about 160°, however, a more vigorous reaction occurs, methyl chloride being liberated and an amidine formed: $NPh{:}CPhCl + C_6H_4Me{\cdot}NMe_2 = NPh{:}CPh{\cdot}NMe{\cdot}C_6H_4Me + CH_3Cl$. Like other amidines, the two prepared in this way form highly stable, sparingly soluble nitrates.

For the preparation of unsymmetrical tetra-alkyldiaminobenzophenones by the above process, *p*-dialkylaminobenzoic acids are required, two different methods for obtaining these acids being employed: (1) *p*-Acetotoluidide is oxidised to *p*-acetaminobenzoic acid, the latter hydrolysed to aminobenzoic acid, and this methylated by means of methyl sulphate; this is a tedious process. (2) The action of carbonyl chloride on dimethyl- (or diethyl-) aniline, which readily yields large quantities of the desired acids (Michler, A., 1876, ii, 68). Preparation of dimethylaminobenzoic acid by oxidation of *p*-dimethylaminobenzaldehyde is impracticable, this aldehyde being either unattacked or completely destroyed by the oxidising agents tried. The use of phosphorus pentachloride for converting large amounts of the acids into their anilides yields products difficult to purify, the best chlorinating agent being carbonyl chloride (Hofmann, *Zeitsch. angew. Chem.*, 1908, **21**, 1986).

Tetranitromethylaminobenzophenone (probably

$$NO_2 : NO_2 : NMe{\cdot}NO_2 : NO_2 = 3 : 5 : 4 : 3'),$$

obtained by nitration of *p*-dimethylaminobenzophenone in the cold by means of fuming nitric acid, forms pale yellow crystals, m. p. 175—175·5°. If benzomethylamide is nitrated similarly but heated finally at 60—70°, it yields tetranitromethylaniline, m. p. 128°, but if concentrated sulphuric and nitric (2 mols.) acids are used, the principal product is dinitrobenzomethylanilide, m. p. 138° (Hess, *loc. cit.*, gave 136°).

Benzomethyl-*o*-toluidide, $C_{15}H_{15}ON$, forms large, colourless crystals, m. p. 79—80°; Fischer (*loc. cit.*) gave m. p. 67° and Lander (T., 1903, **81**, 408) m. p. 65—66°.

Diethylaminobenzophenone has m. p. 79—81°, which is somewhat higher than the value previously given.

Methyl-o-*toluidinophenyliminophenylmethane*,

$$C_6H_4Me\cdot NMe\cdot CPh:NPh,$$

forms pale yellow crystals, m. p. 95°; the *hydrochloride*, m. p. 250° (decomp.) and *nitrate*, m. p. 207° (decomp.), were analysed.

p-*Diethylaminobenzanilide*, $C_{17}H_{20}ON_2$, crystallises in shining scales or slender needles, m. p. 122—123°.

4 : 4′-Dimethyldiethyldiaminobenzophenone, m. p. 93—95°, gives a *picrate*, $C_{19}H_{24}ON_2,C_6H_3O_7N_3$, m. p. 178·5°.

Methyl-o-*toluidinophenylimino*-p-*dimethylaminophenylmethane*,

$$C_6H_4Me\cdot NMe\cdot C(NPh)\cdot C_6H_4\cdot NMe_2,$$

forms colourless crystals, m. p. 132°. T. H. P.

Di- and Tri-phenylmethane Series. II. Unsymmetrical Leuco-bases of the Malachite-green and Crystal-violet Series. JAKOB MEISENHEIMER, EUGEN VON BUDKEWICZ, GEORG KANANOW, and JULIUS NERESHEIMER (*Annalen*, 1921, **423**, 95—105).—The unsymmetrical aminobenzophenones described in the preceding paper form the starting points for obtaining dissimilarly-substituted colouring matters of the malachite-green and crystal-violet series. By means of phosphoryl chloride *p*-dimethylaminobenzophenone and diethylaniline are condensed to a colouring matter which does not crystallise, but yields the crystalline leuco-base, 4 : 4′-dimethyldiethyldiaminotriphenylmethane; the leuco-base could not be oxidised to the colouring matter, and the corresponding carbinol did not crystallise. Condensation of *p*-diethylaminobenzophenone and dimethylaniline yield the same colouring matter, tetramethyldiaminodiphenylmethane being also obtained.

p-Dimethylaminobenzophenone and dipropylaniline condense to a crystalline colouring matter, which yields on reduction the crystalline leuco-base, 4 : 4′ : 4″-tetramethyldipropyltriaminotriphenylmethane; the corresponding carbinol also crystallises. On the other hand, attempts to condense *p*-dimethylaminobenzophenone and dimethyl-*o*-toluidine to hexamethylrosaniline proved unsuccessful; at 100°, a very small proportion of colouring matter is formed, but at higher temperatures the product consists of a compound which is virtually insoluble in all solvents and was not investigated.

The benzhydrols, obtained by reduction of the benzophenones, condense more readily than the latter with tertiary amines, leuco-bases then being obtained directly; various compounds have been prepared in this way. Bielecki and Koleniew's statement that 4 : 4′ : 4″-hexamethyltriamino-5″-methyltriphenylmethane may be obtained from dimethylaminobenzhydrol and dimethyl-*o*-toluidine (A., 1908, i, 697) is confirmed, double the yields given by these authors being obtained.

4 : 4′-Dimethyldiethyldiaminobenzhydrol, $C_{19}H_{26}ON_2$, obtained by reducing dimethyldiethyldiaminobenzophenone by means of alcohol and sodium amalgam, forms colourless crystals, m. p. 61°, and is highly unstable, rapidly becoming green and deliquescing.

4 : 4′-Dimethyldiethyldiaminotriphenylmethane, $C_{25}H_{30}N_2$, forms snow-white crystals, m. p. 65—67°, turns green in the air, and forms crystalline double salts with zinc, tin, and platinum chlorides. The carbinol base, prepared by the action of lead peroxide in hydrochloric or acetic acid solution, is a brownish-yellow oil.

The carbinol corresponding with malachite-green has m. p. 107—107·5°; Doebner (A., 1883, 861) gave m. p. 132° and Villiger and Kopetschni (A., 1912, i, 1030) 109—110° or 120—122°, according to the solvent used; the authors were, however, unable to confirm this dimorphism.

4 : 4′ : 4″-*Tetramethyldipropyltriaminotriphenylmethane*, $C_{29}H_{39}N_3$, forms colourless crystals, m. p. 98°, turns green in the air, and yields a blue colouring matter when oxidised with lead peroxide.

4 : 4′ : 4″-*Tetramethyldiethyltriaminotriphenylmethane*, $C_{27}H_{35}N_3$, crystallises in colourless needles, m. p. 141°, and turns yellow in the air.

4 : 4′ : 4″-*Dimethyldiethyldipropyltriaminotriphenylmethane*, prepared either by condensation of dimethyldiethyldiaminobenzophenone with dipropylaniline and subsequent reduction or from the benzhydrol and dipropylaniline, is a yellow oil, and yields no crystallisable salt; the colouring matter and the carbinol also do not crystallise.

4 : 4″ - *Tetramethyl*-4′ - *diethyltriamino*-5″ - *methyltriphenylmethane*, $C_{28}H_{37}N_3$, obtained from dimethyldiethyldiaminobenzhydrol and dimethyl-*o*-toluidine, forms colourless crystals, m. p. 132—133°.

4-*Dimethylaminophenyl*-4-*dimethylamino*-α-*naphthylphenylmethane*, $C_{27}H_{28}N_2$, prepared from dimethylaminobenzhydrol and dimethyl-α-naphthylamine, forms a red, crystalline powder, sintering at 95°, m. p. 105°, and in organic solvents forms solutions showing blue fluorescence.

When prepared by the method described by Baeyer and Villiger (A., 1902, i, 380), trianisylmethane is accompanied by *tetra-anisylmethane*, $C_{25}H_{16}(OMe)_4$, m. p. 115—115·5°; pure trianisylmethane, m. p. 47·5°, crystallises well and exhibits no tendency to separate as an oil. T. H. P.

Di- and Tri-phenylmethane Series. III. Attempts to Prepare Optically Active Leuco-bases of Triphenylmethane Colouring Matters. JAKOB MEISENHEIMER and JULIUS NERESHEIMER (*Annalen*, 1921, **423**, 105—118).—The authors have made attempts to resolve unsymmetrical leuco-bases of the triphenylmethane series, containing an asymmetric carbon atom, into optically active forms. If Rosenstiehl's formula for triphenylmethane colouring matters is accurate, such active leuco-bases should yield active colouring matters when oxidised; disappearance of the optical activity on oxidation would, however, support the quinonoid structure for the triphenylmethane colouring matters, although the possibility of racemisation exists. The compounds investigated consisted of (1) the α-bromocamphor-π-sulphonates of various leuco-bases, and (2) the quinine, brucine, and coniine salts of 4 : 4′-dimethyldiethyldiaminotriphenylmethanesulphonic acid.

In no case, however, could resolution into optical antipodes be achieved. The following compounds were prepared:

4 : 4′ : 4″-*Tetramethyldiethyltriaminotriphenylmethane dimethiodide*, $C_{29}N_{41}N_3I_2$. 4 : 4′-*Dimethyldiethyldiaminotriphenylmethane monomethiodide*, $C_{26}H_{33}N_2I$, colourless needles, sintering at 148°, m. p. 153° (decomp.); *dimethiodide*, $C_{27}H_{36}N_2I_2 + CH_3{\cdot}OH$, needles, sintering at 178°, m. p. 188° (decomp.); the *α-bromocamphor-π-sulphonate*, $C_{36}H_{47}O_4N_2SBr(+C_6H_6)$, forms pale red, nodular aggregates of slender needles. *4-Dimethylaminophenyl-4-dimethylamino-1-naphthylphenylmethane methiodide*, $C_{28}H_{31}N_2I + CH_3{\cdot}COMe$, shining crystals.

Dimethyldiethyldiaminotriphenylmethanesulphonic acid,

$$C_{25}H_{30}O_3N_2S,$$

m. p. 225—230°; its *sodium* salt, $+$ Et·OH, m. p. about 260° (decomp.); *quinine* salt, $C_{25}H_{30}O_3N_2S,C_{20}H_{24}O_2N_2$, m. p. varying between 225—227° and 214—216°; *brucine* salt, and *coniine* salt were analysed. The *sodium* salt of the corresponding *carbinolsulphonic acid*, obtained by oxidising the above sulphonic acid by means of lead peroxide, forms colourless crystals, which rapidly turn dark green in the air and light. The *sulphonic* acid of *leuco-malachite-green*, m. p. 240—245°, behaves similarly to that of the unsymmetrical leuco-base. T. H. P.

Preparation of Quinolyl Ketones. VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.P. 330945; from *Chem. Zentr.*, 1921, ii, 603—604. An addition to D.R.P. 268830, A., 1914, i, 575).—The use of esters containing an *N*-acylated basic residue, R, in place of esters of the general formula $R^I{\cdot}CH_2{\cdot}CO_2R^{II}$ with an alkyl R^I as indicated in the first patent, is claimed. A quinolyl ketone, $NH{<}\begin{matrix}CH_2-CH_2\\CH_2{\cdot}CHEt\end{matrix}{>}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_9NH_6$, is prepared by the condensation of ethyl *N*-benzoylhomocincholeuponate,

$$NBz{<}\begin{matrix}CH_2-CH_2\\CH_2{\cdot}CHEt\end{matrix}{>}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$$

with ethyl quinoline-4-carboxylate in the presence of sodium ethoxide at about 80° to the oily ketonic *ester*,

$$NBz{<}\begin{matrix}CH_2-CH_2\\CH_2{\cdot}CHEt\end{matrix}{>}CH{\cdot}CH_2{\cdot}CN(CO_2Et){\cdot}CO{\cdot}C_9H_6N$$

which is converted by boiling hydrochloric acid (17%) into the ketone, benzoic acid, carbon dioxide, and alcohol. The ketone is identical with dihydrocinchotoxine, since it gives the well-known colorations with diazobenzene–sulphonic acid and nitrobenzene containing nitrothiophen and is transformed by introduction of bromine and subsequent elimination of hydrogen bromide into dihydrocinchoninone, m. p. 138°, $[\alpha]_D^{18} + 76{\cdot}45°$ in absolute alcoholic solution (final value). H. W.

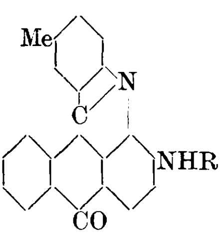
***spiro*-Pyrimidines. I. *cyclo*Butane-1 : 5-*spiro*pyrimidines.** ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1921, **43**, 677—684).—The yield of ethyl *cyclo*butanedicarboxylate from trimethylene dibromide and ethyl sodiomalonate (Perkin, T., 1887, **51**, 449) is increased to 42% by gradual addition of

the latter to an alcoholic solution of the dibromide at 78° kept well stirred. The *amide*, $C_6N_{10}N_2O_2$, forms needles, m. p. 278°. By condensation of the ester with carbamide, guanidine, their derivatives, and benzamidine in presence of sodium ethoxide, etc., *spiro*-pyrimidines are obtained.

cyclo*Butane*-1 : 5-spiro-2 : 4 : 6-*triketohexahydropyrimidine*, $C_7H_8O_3N_2$, scales, m. p. 258°, from carbamide has a bitter taste resembling that of veronal; cyclo*butane*-1 : 5-spiro-2 : 4 : 6-*triketo*-1-*methylhexahydropyrimidine*, $C_8H_{10}O_3N_2$, plates, m. p. 170°, from methylcarbamide; cyclo*butane*-1 : 5-spiro-2 : 4 : 6-*triketo*-1-*ethylhexahydropyrimidine*, $C_9H_{12}O_3N_2$, scales, m. p. 135°, from ethylcarbamide; cyclo*butane*-1 : 5-spiro-2 : 4 : 6-*triketo*-1-*phenylhexahydropyrimidine*, $C_{13}H_{12}O_3N_2$, needles, m. p. 225°, from phenylcarbamide; cyclo*butane*-1 : 5-spiro-2 : 4 : 6-*triketo*-1-*benzylhexahydropyrimidine*, $C_{14}H_{14}O_3N_2$, needles, m. p. 131°, from benzylcarbamide; cyclo*butane*-1 : 5-spiro-1-*amino*-2 : 4 : 6-*triketohexahydropyrimidine*, $C_7H_9O_3N_3$, m. p. 262° (decomp.), from semicarbazide; cyclo*butane*-1 : 5-spiro-2-*imino*-4 : 6-*diketohexahydropyrimidine*, $C_7H_9O_2N_3$, not melting at 300°, from guanidine; cyclo*butane*-1 : 5-spiro-2-*cyanimino*-4 : 6-*diketohexahydropyrimidine*, $C_8H_8O_2N_4$, not melting at 300°, from dicyanodiamide; cyclo*butane*-1 : 5-spiro-2-*thio*-4 : 6-*diketohexahydropyrimidine*, m. p. 240°, from thiocarbamide; cyclo*butane*-1 : 5-spiro-4 : 6-*diketo*-2-*phenyltetrahydropyrimidine*, $C_{13}H_{12}O_2N_2$, m. p. 263°, yellow and microcrystalline, from benzamidine.

J. K.

Preparation of Nitrogenous Derivatives of Anthracene. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 330572; from *Chem. Zentr.*, 1921, ii, 559).—Alizarin or such derivatives of alizarin as contain one or more additional hydroxyl groups in heteronuclear substitution (with the exception of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone–alizarin bordeaux) is heated at a high temperature with primary aromatic amines or their substitution products with or without the addition of stannous chloride. Alizarin, aniline, and stannous chloride at 170—180° yield *phenylaminocœramidonine* (annexed formula), shining needles, m. p. 203—205°; alizarin, *p*-toluidine, and stannous chloride give a *compound*, m. p. 198—199°. 1 : 2 : 6-Trihydroxyanthraquinone, *p*-toluidine, and stannous chloride yield *hydroxy* p-*toluidinomethylcœramidonine*, m. p. 284—287°. 1 : 2 : 7-Trihydroxyanthraquinone gives two *compounds* with *p*-toluidine and stannous chloride, one of which is soluble in sodium hydroxide solution, whereas the other is insoluble and forms dark crystals, m. p. above 340°. Under similar conditions, 1 : 2 : 5-trihydroxyanthraquinone yields *compounds*, m. p. 213—215° and above 300°, which are readily and very sparingly soluble in acetone respectively. 1 : 2 : 5 : 6-Tetrahydroxyanthraquinone, *p*-toluidine, and stannous chloride give *compounds*, one of which has m. p. 248—250° and is freely soluble in acetone, in which the other



dissolves very sparingly. The products, which are termed *arylaminocœramidonines*, are used as dyes, or as initial materials in the preparation of the latter. The sulphonic acids dye unmordanted wool in red, violet, or blue shades. H. W.

Reaction of the Formamidines. VIII. Some Thiazolidone Derivatives. F. B. DAINS, ROY IRVIN, and C. G. HARREL (*J. Amer. Chem. Soc.*, 1921, **43**, 613—618. Compare A., 1916, i, 751).—Further illustrations are given of the reactivity in 4-thiazolidones of the methylene group of the complex $CO\cdot CH_2\cdot S$ towards benzaldehyde and formamidines. The thiazolidones employed were prepared by boiling di-arylthiocarbamides with chloroacetic acid in alcoholic solution in presence of pyridine. Acid hydrolysis of the products gives thiazolediones, which are therefore the chief products if the original condensation be performed in absence of pyridine. When mixed diarylthiocarbamides are employed, only one product results in place of the two theoretically possible.

2-m-*Tolylimino*-3-m-*tolyl*-4-*thiazolidone*, $CH_2<\begin{matrix} S—C:N\cdot C_7H_7 \\ CO\cdot N\cdot C_7H_7 \end{matrix}$, yellow prisms, m. p. 154—155°, from di-*m*-tolylthiocarbamide (5-*benzylidene* derivative, $C_{24}H_{20}ON_2S$, yellow needles, m. p. 175—177°). 2-p-*Tolylimino*-3-p-*tolyl*-4-*thiazolidone*, $C_{17}H_{16}ON_2S$, yellow prisms, m. p. 127° (*hydrochloride*, $C_{17}H_{16}ON_2S,HCl$, m. p. 195—205°, decomp.; 5-*benzylidene* derivative, $C_{24}H_{20}ON_2S$, yellow needles, m. p. 197°, hydrolysed by potassium hydroxide to 3-p-*tolyl*-5-*benzylidene*-2 : 4-*thiazoledione*, $C_{17}H_{13}O_2NS$, needles, m. p. 210°; 5-*anilinomethylene* derivative, $C_{24}H_{21}ON_3S$, yellow needles, m. p. 168°, by condensation with diphenyl formamidine; 5-β-*naphthylaminomethylene* derivative, $C_{28}H_{23}ON_3S$, m. p. 215°). 2-p-*Bromophenylimino*-3-p-*bromophenyl*-4-*thiazolidone*, $C_{15}H_{10}ON_2Br_2S$, m. p. 183° (5-*benzylidene* derivative, $C_{22}H_{14}ON_2Br_2S$, yellow crystals, m. p. 220°; 5-β-*naphthylaminomethylene* derivative, $C_{26}H_{17}ON_3Br_2S$, yellow needles, m. p. 190°). 2-p-*Chlorophenylimino*-3-p-*chlorophenyl* 4-*thiazolidone*, $C_{15}H_{10}ON_2Cl_2S$, yellow crystals, m. p. 165° (5-*benzylidene* derivative, $C_{22}H_{14}ON_2Cl_2S$, greenish-yellow needles, m. p. 213°; 5-β-*naphthylaminomethylene* derivative, $C_{26}H_{17}ON_3Br_2S$, greenish-yellow crystals, m. p. 204°). 2-*Phenylimino*-3-p-*bromophenyl*-4-*thiazolidone*, $C_{15}H_{11}ON_2BrS$, prisms, m. p. 175—176° (5-*benzylidene* derivative, $C_{22}H_{15}ON_2BrS$, yellow plates, m. p. 197—199°). 2-*Phenylimino*-3-m-*bromophenyl*-4-*thiazolidone*, $C_{15}H_{11}ON_2BrS$, m. p. 171° (5-*benzylidene* derivative, $C_{22}H_{15}ON_2BrS$, pale yellow needles, m. p. 200—201°). 2-*Phenylimino*-3-p-*chlorophenyl*-4-*thiazolidone*, $C_{15}H_{11}ON_2ClS$, prisms, m. p. 184—185° (5-*anilinomethylene* derivative, $C_{22}H_{16}ON_4Cl$, yellow needles, m. p. 180°). 2-*m*-Nitrophenylimino-3-phenyl-4-thiazolidone could not be purified for analysis, but gave a 5-*benzylidene* derivative, $C_{22}H_{15}O_3N_3S$, yellow crystals, m. p. 193°.

3-p-*Bromophenyl*-2 : 4-*thiazoledione*, $C_9H_6O_2NBrS$, needles, m. p. 130°, by hydrolysis of 2-*p*-bromophenyl- or 2-phenyl-imino-3-*p*-bromophenyl-4-thiazolidone : 3-p-*chlorophenyl*-2 : 4-*thiazoledione*, $C_9H_6O_2NClS$,

needles, m. p. 136—137°, were prepared from the analogous compounds. J. K.

Synthesis of Dicyano-*o*-phenyleneguanidine from *o*-Phenylenediamine. GUIDO PELLIZZARI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 39—44; *Gazzetta*, 1921, **51**, 140).—It has been previously shown by Pellizzari and Gaiter (A., 1919, i, 134) that the action of cyanogen bromide on phenylhydrazine results in the replacement of the three basic hydrogen atoms by three cyanogen groups, the tricyanophenylhydrazine which should be formed then undergoing intramolecular change into αβ-dicyano-*o*-phenyleneguanidine. Gradual hydrolysis of the latter yields, in order, β-cyano-*o*-phenyleneguanidine, *o*-phenylene-β-guanylcarbamide, and *o*-phenyleneguanidine. As regards the synthesis of these compounds from *o*-phenylenediamine, *o*-phenyleneguanidine was obtained from cyanogen bromide and phenylenediamine (Pierron, A., 1908, i, 925) and by further cyanation, Pellizzari and Gaiter (*loc. cit.*) introduced a cyanogen group into the α-position, but not into the β-position. When, however, the first product of the hydrolysis of αβ-dicyano-*o*-phenyleneguanidine, namely, β-cyano-*o*-phenyleneguanidine, is converted into its sodium salt and this is treated with cyanogen bromide, αβ-dicyano-*o*-phenyleneguanidine is obtained (see Pellizzari, A., 1919, i, 201). Since β-cyano-*o*-phenyleneguanidine may be obtained, by way of phenylenediguanide, from *o*-phenylenediamine, the synthesis from the latter of αβ-dicyano-*o*-phenyleneguanidine is complete.

From *o*-phenylenediamine hydrochloride and dicyanodiamide, Ziegelbauer (A., 1897, i, 142) obtained a phenylenediguanide to which he ascribed the formula $C_6H_4<{NH\cdot C(:NH) \atop NH\cdot C(:NH)}>NH$. The author has now obtained this compound by the following series of reactions, which lead to a constitution different from that given by Ziegelbauer: $C_6H_4<{\overline{\quad\quad}N \atop N(CN)}>C\cdot NH\cdot CN + NH_3 \longrightarrow$

$$\begin{matrix} N\!=\!\!=\!C\cdot NH\!-\!\!-\!C:NH \\ C_6H_4\cdot N\cdot C(NH)\cdot NH \end{matrix} + H_2O \longrightarrow \begin{matrix} N\!=\!\!=\!C\cdot NH\cdot C:NH \\ C_6H_4\cdot N\cdot CO\!-\!NH \end{matrix} + 2H_2O \longrightarrow$$

$C_6H_4<{\overline{\quad}N \atop NH}>C\cdot NH\cdot C(:NH)\cdot NH_2$. This structure is confirmed by the ready hydrolysis of the compound to *o*-phenylene-β-guanylcarbamide (Pellizzari and Gaiter, *loc. cit.*), and it is evident that the formation of phenylenediguanide from *o*-phenylenediamine and dicyanodiamide is represented by the equation $NH_2\cdot C_6H_4\cdot NH_2 + CN\cdot NH\cdot C(NH)\cdot NH_2 = NH_3 + C_6H_4<{\overline{\quad}N \atop NH}>C\cdot NH\cdot C(NH)\cdot NH_2$. When treated with nitrous acid, this phenylenediguanide does not yield *o*-phenyl-β-guanylcarbamide, but loses the elements of ammonia with formation of β-cyano-*o*-phenyleneguanidine in good yield. This new reaction of nitrous acid, in which a guanidine residue is transformed into a cyanamide residue, renders possible the direct synthesis of dicyanophenyleneguanidine from *o*-phenylenediamine, thus: (1) *o*-phenylenediamine and dicyanodiamide

give phenylenediguanide, (2) the latter and nitrous acid give β-cyanophenyleneguanidine, and (3) the potassium salt of the latter with cyanogen bromide yields dicyanophenyleneguanidine:

$$NH_2\cdot C_6H_4\cdot NH_2 \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{-N-}{NH}>C\cdot NH\cdot C(NH)\cdot NH_2 \rightarrow$$

$$C_6H_4<\genfrac{}{}{0pt}{}{-N-}{NH}>C\cdot NH\cdot CN \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{-N-}{N(CN)}>C\cdot NH\cdot CN.$$

The product thus obtained is identical with that from phenylhydrazine and cyanogen bromide.

o-Phenylenediguanide, obtained impure by Ziegelbauer (*loc. cit.*) crystallises in shining, nacreous laminæ, decomposing at 254°. Its other properties and its salts are described in a paper to be published later. T. H. P.

Relations between Azoxy-derivatives and Diazo-compounds. A. Angeli (*Gazzetta*, 1921, **51**, i, 35—42).—The author has investigated the behaviour towards oxidising agents (compare A., 1917, i, 417) of various azoxyphenols of the form $C_6H_5\cdot N_2O\cdot C_6H_4\cdot OH$. The para-substituted derivatives exist in two isomeric forms, namely, $Ph\cdot NO\colon N\cdot C_6H_4\cdot OH$, m. p. 156°, and $NPh\colon NO\cdot C_6H_4\cdot OH$, m. p. 118° (compare A., 1914, i, 882), the former being identical with that obtained in small proportion by the action of alkalis on nitrosobenzene (Bamberger, A., 1900, i, 531; 1902, i, 505).

The isomeride, m. p. 156°, is readily oxidised in alkaline solution by means of 2% permanganate solution in accordance with the equation $Ph\cdot NO\colon N\cdot C_6H_4\cdot OH \rightarrow C_6H_5\cdot N_2\cdot OH$, the isolation of intermediate compounds, such as $Ph\cdot NO\colon N\cdot CO_2H$ or $Ph\cdot NO\colon N\cdot CO\cdot CO_2H$, not being found possible. The isomeride, m. p. 118°, is, on the other hand, attacked only with difficulty by permanganate, the resulting solution exhibiting the reactions of *iso*diazo-compounds. This difference in the behaviour of isomeric azoxyphenols towards oxidising agents is similar to that observed when the corresponding para-halogenated isomerides are treated with either bromine or nitric acid; thus, the compound $Ph\cdot NO\colon N\cdot C_6H_4Br$, exhibits great resistance, whereas the isomeride, $NPh\colon NO\cdot C_6H_4Br$, readily undergoes substitution in the phenyl group by bromine or by the nitro-group. Application of these considerations to the two isomeric *o*-hydroxyazoxybenzenes which were regarded by Bamberger as stereoisomerides, indicates that these compounds are really the structural isomerides, $Ph\cdot NO\colon N\cdot C_6H_4\cdot OH$, m. p. 76°, and $NPh\colon NO\cdot C_6H_4\cdot OH$, m. p. 108°, the former being the more readily oxidised by alkaline permanganate.

Oxidation by means of alkaline permanganate of *pp'*-azoxyphenol, obtainable by treating the corresponding azo-compound with hydrogen peroxide in acetic acid solution, yields no compounds giving diazo-derivatives with β-naphthol; the resulting solution contains much potassium oxalate, but no indication is obtained of the formation of azoxydicarboxylic acid, which would be unstable. The oxidation of *p*-azophenol by means of permanganate yields traces of an *iso*diazo-compound, doubtless derived from the azoxy-compound originally formed.

These transformations show the close analogy existing between aromatic azoxy-derivatives and diazo-compounds, and render it probable that the oxidation of azoxy-compounds may be represented by the scheme: $Ph\cdot N_2O\cdot C_6H_4\cdot OH \rightarrow Ph\cdot N_2O\cdot CO_2H \rightarrow NPh\colon N\cdot OH$.

These and other similar results indicate that the differences in behaviour of normal and of *iso*diazo-compounds, which Hantzsch regarded as due to differences in configuration (A., 1894, i, 453) are explained satisfactorily on the hypothesis of structural isomerism. T. H. P.

Azopyrroles. I. R. CIUSA (*Gazzetta*, 1921, **51**, i, 49—55).—In azobenzene solution, benzeneazopyrrole exhibits abnormally high depressions of the freezing point, so that, since pyrrole forms solid solutions with benzene, it appears that benzeneazopyrrole in its azo-form (compare Plancher and Soncini, A., 1903, i, 449) apparently gives solid solutions with azobenzene. As regards the pyrrolene-hydrazonic form of benzeneazopyrrole, $C_4H_3N\colon N\cdot NHPh$, although the two groups, NPh and NHPh, may be isomorphogenic, the groups NPh and $C_4H_3N\colon N$ are certainly not so. Similar conclusions are drawn by comparison of the absorption spectra of the following compounds in alcoholic solution: benzeneazopyrrole, *o*-, *m*-, and *p*-nitrobenzeneazopyrroles and *p*-nitrobenzeneazo-1-methylpyrrole; for the visible portion of the spectrum, to which the measurements were confined, these compounds exhibit similar absorption curves, and since the last of the compounds is necessarily of azoic structure, the conclusion is drawn that the others also have this constitution. [BOERIS: Benzeneazopyrrole forms monoclinic crystals, $a:b:c = 1{\cdot}3622:1:1{\cdot}0596$, $\beta = 83°\ 2'$, and thus shows no analogy in crystalline form with azobenzene, which also crystallises in the monoclinic system, $a:b:c = 2{\cdot}10756:1:1{\cdot}33123$, $\beta = 65°\ 34'$]. To the alkali salts of *o*- and *p*-nitrobenzeneazopyrrole, however, pyrrolenic constitutions must be assigned, addition of alcoholic potassium hydroxide to the acetone solutions of these compounds producing a pronounced alteration in colour similar to that obtained with *o*- and *p*-nitrophenylhydrazones, for salts of which a quinonoid structure must be assumed; with the meta-derivatives, the acetone solution is scarcely darkened, so that the proportion of meta-quinonoid salt is small, as should be the case in view of the difficulty of formation of meta-quinones. *p*-Nitrobenzeneazo-1-methylpyrrole, which has a fixed azoic constitution and hence cannot form the nitronic acid, does not change in colour on addition of alcoholic potassium hydroxide.

p-*Nitrobenzeneazopyrrole*, $C_{10}H_8O_2N_4$, forms acicular, orange crystals, m. p. 148—149°, and dissolves in concentrated sulphuric or hydrochloric acid, giving an orange-yellow solution. The *meta*-isomeride forms pale yellow needles, m. p. 91—92°, and, even in traces, yields a lemon-yellow coloration with sulphuric acid. The *ortho*-isomeride crystallises in long, orange-yellow needles, m. p. 121—122°, and gives an orange-yellow coloration with sulphuric acid.

p-*Nitrobenzeneazo*-1-*methylpyrrole*, $C_{11}H_{10}O_2N_4$, forms violet scales

with metallic reflection and yields an orange-yellow coloration with either concentrated sulphuric or hydrochloric acid. Addition of cold water to its alcoholic solution causes the separation of a yellow form, whilst, if hot water is added, a reddish-violet form separates, these two modifications being chromoisomeric forms.

T. H. P.

Physico-chemical Investigations on so-called Hydroxyazo-compounds. E. PUXEDDU and M. GENNARI (*Gazzetta*, 1921, **51**, i, 147—152).—The authors have measured, by the telephonic method, the molecular conductivities at 25° of the sodium and potassium salts of *p*-hydroxyazobenzene, benzeneazo-*o*-, *m*-, and *p*-cresols, and *o*-, *m*-, and *p*-tolueneazophenols. Trustworthy results have, however, been obtained only for the salts of *o*-tolueneazophenol, solutions of the other compounds in the equivalent amounts of alkali hydroxide solutions not being obtainable.

The alkali salts of the hydroxyazo-compounds exhibit the phenomenon of hydrolysis. The value of $\Delta_{1024-32}$ for the sodium derivative of *o*-tolueneazophenol is 14·12, which is somewhat higher than the average, whilst for the sodium salt of benzeneazo-*o*-cresol the value of Δ is very low. For the potassium salts the values of Δ are about 20. T. H. P.

Stability of Tautomeric Formaldehydephenylhydrazones. NEVIL VINCENT SIDGWICK and ELINOR KATHARINE EWBANK (T., 1921, 1919, 486—492).

Reduction of Oxyhæmocyanin, and the Compound of Hæmocyanin with Nitric Oxide. CH. DHÉRÉ and A. SCHNEIDER (*Compt. rend. Soc. Biol.*, 1920, **83**, 1505—1507; from *Chem. Zentr.*, 1921, i, 453).—The investigations were made on the blood of crayfish, crab, and cuttle-fish. Here, as in the case of the snail and lobster, complete reduction occurs on aeration with an indifferent gas, also by exhaustion and heating.

A green compound was formed with nitric oxide in the case of snail hæmocyanin, but not in that of lobster hæmocyanin. In the case of crayfish, the compound is formed in small quantities by long passage of the gas. Larger quantities are formed in the case of the cuttle-fish. Preparations from snail hæmocyanin gradually assumed a more or less yellow colour. G. W. R.

A Method of Purifying certain kinds of Proteins. ADA M. FIELD (*J. Amer. Chem. Soc.*, 1921, **43**, 667—668).—The proteins are recognised to possess amphoteric properties (Michaels, A., 1910, i, 646; Loeb, A., 1919, i, 295). Hence any protein with isoelectric point at a hydrogen-ion concentration greater than that of water will lose any combined basic elements when dialysed for a sufficient length of time against dilute acid, and the resulting acid-protein compound can then be completely converted into protein by dialysis against water. Gelatin purified by this pro-

cedure forms an opaque, white jelly, free from ash. Similarly, proteins with isoelectric points less than that of water in respect of hydrogen ions may be successively treated with dilute alkali and water. J. K.

Ion Series and the Physical Properties of Proteins. III. Action of Salts in Low Concentration. JACQUES LOEB (*J. Gen. Physiol.*, 1921, **3**, 391—414).—The Hofmeister series, which arranges ions according to their lyotropic effect (for example, on the swelling, osmotic pressure, and viscosity of gelatin), "is the result of an error due to the failure to notice the influence of the addition of a salt upon the hydrogen-ion concentration of the protein solution. As a consequence of this failure, effects caused by a variation in the hydrogen-ion concentration of this solution were erroneously attributed to differences in the nature of the ions." The relative depressing effect of the ions on swelling, osmotic pressure, and viscosity is a function only of the valency and sign. Ions of the same charge and valency have practically the same depressing effect on gelatin solutions of the same P_H. With increase in the ionic valency the effect increases rapidly. With solutions stronger than $M/16$ it is unsafe to draw conclusions concerning the specific effects of the ions, since at that concentration the values of these properties are near the minimum characteristic of the isoelectric point.

The experiments relate to hydrochloric acid, sodium, potassium, calcium, and lanthanum chlorides, potassium hydroxide, and sodium ferrocyanide, acetate, oxalate, and sulphate, and sodium dihydrogen phosphate, and chiefly to their effect on the viscosity of gelatin (compare the following abstract for references). G. B.

Chemical and Physical Behaviour of Casein Solutions. JACQUES LOEB (*J. Gen. Physiol.*, 1921, **3**, 547—555).—It is found that chemically equivalent amounts of hydrochloric and phosphoric acids, potassium, sodium, calcium, and barium hydroxides are required to bring 1% solutions of isoelectric casein to the same P_H. Casein apparently therefore combines with these acids and bases in molecular proportions, to give definite chemical compounds.

Determinations of the osmotic pressure and viscosity, in relation to the P_H, of solutions of these casein salts were carried out; the curves thus obtained are almost identical in the case of the chloride and phosphate; the curves for sodium and potassium caseinate are identical, as are also those for calcium and barium caseinate; there is, however, a considerable difference in the height of the curves for the salts with univalent and bivalent kations.

It is concluded therefore that it is the valency and not the nature of the combining ion which determines the effect on the physical properties of casein solutions. These results bear out those previously obtained with regard to egg-albumin and gelatin (compare A., 1918, i, 318, 510; 1919, i, 295, 296, 418; ii, 14; 1920, i, 104, 894; this vol., i, 136). C. R. H.

The Colloidal Behaviour of Proteins. JACQUES LOEB (*J. Gen. Physiol.*, 1921, **3**, 557—564).—Previous theories to account for the depressant effect of neutral salts on the physical properties of solutions of protein–acid salts are briefly discussed. It is suggested that the explanation may be found in the Donnan equilibrium (T., 1911, **99**, 1554; 1919, **115**, 1313). Experiments are described in which gelatin chloride solutions (P_H 3·5) containing varying concentrations of sodium nitrate, in collodion bags, were placed in aqueous hydrochloric acid solutions (P_H 3·0) containing similar concentrations of sodium nitrate. It was found that increasing concentrations of the neutral salt depressed the potential difference between the two solutions in the same proportion in which it depressed the osmotic pressure of the gelatin chloride solution.

The observed values of the potential difference agree with those calculated from Nernst's formula, assuming the effect to be due to differences in P_H.

Similar results were obtained with regard to the swelling phenomena of gelatin.

A close resemblance was observed between the curves representing osmotic pressure and potential difference as functions of the P_H in the case of gelatin chloride, sulphate, phosphate, and oxalate. In all these cases the observed values of the potential difference agreed fairly well with those calculated from the Nernst formula (compare A., 1920, ii, 14, 234, 358, 476, 477, 602). C. R. H.

Amylase; its Estimation and the Mechanism of its Action. L. AMBARD (*Bull. Soc. Chim. Biol.*, 1921, **3**, 51—65).—Crude powdered starch removes amylase from solution and keeps it fixed, in spite of repeated washing by the centrifuge. On the other hand, it gives up the ferment promptly to filtered starch or glycogen solutions containing neutral salt; the latter process the author terms "défixation." It furnishes (1) a convenient method for estimating amylase (in saliva, blood, urine, etc.), and (2) important light on the theory of its action. It is shown that the whole (96—100%) of the ferment in a solution can be removed by starch powder; for purposes of estimation, the solid starch–ferment complex is mixed with filtered starch solution containing sodium chloride (to allow of defixation) and a phosphate mixture (to ensure the optimum P_H 6·60 for the action of the ferment). The mixture is kept at 35° for a time, until not more than one-tenth of the starch has been hydrolysed; during this initial phase of the reaction the amount of sugar formed is proportional to the time (that is, the rate of the reaction is constant). The ferment action is then stopped by addition of enough sodium hydroxide to overcome the buffer action of the phosphate, and the maltose formed is estimated by a modification of Bertrand's process (this vol., ii, 220). The method is evidently very accurate.

As regards the theoretical aspect, the author could not establish whether solid starch requires salt for the fixation of amylase, because it could not be washed free from salt; salt added to washed

starch increased the fixation by 1·5% only. The addition of salt, lævulose, sucrose, maltose, glycerol, or inulin to the wash water makes no difference; the amylase remains fixed. Ferric and aluminium hydroxide alone simulate the action of glycogen and starch solutions by reducing the activity of the starch powder–amylase complex, but apparently not by removing any amylase; rather by forming a complex with the starch which partly inhibits the action of the ferment. Salt-free glycogen "defixes" only 4%, but on addition of salt 98%. The change of P_H from 6·60 to 5·0, or to 8·04, had no effect on defixation, but caused in either case a fall of 40% in the hydrolysis. Of this 40% only 2·5% is due to destruction of the enzyme; the decreased hydrolysis is almost entirely due to a slower rate of enzyme action.

These results confirm the hypothesis of Henri (A., 1906, ii, 13; compare also, for example, Bierry and Giaja, A., 1906, ii, 780), that ferment action is preceded by the formation of a complex with the substrate, which formation requires the presence of electrolytes. The author does not, however, confirm the dependence of adsorption on hydrogen-ion concentration. The phenomenon, first observed by Duclaux, that an increase in the concentration of a starch solution beyond about 1% does not increase the rate of hydrolysis seems to depend on the fact that at such a concentration practically all the ferment (98%) is already fixed and employed in hydrolysis. G. B.

Activity of Phytase as Determined by the Specific Conductivity of Phytin–Phytase Solutions. F. A. Collatz and C. H. Bailey (*J. Ind. Eng. Chem.*, 1921, **13**, 317—318).—The change in the specific electrical conductivity of an aqueous solution containing phytin and phytase furnishes a convenient measure of the progress of the hydrolysis of the phytin. The phytase prepared from wheat bran appears to effect the most complete hydrolysis of the phytin at about 55°, although at 60° the action is more rapid during the first fifteen minutes. T. H. P.

Chemistry of Enzymes. Th. Bokorny (*Allgem. Brau. Hopfenzeit.*, 1920, 705—706, 713—714; from *Chem. Zentr.*, 1921, i, 372).—From the fact that enzymes evolve nitrogen with nitrous acid, their amino-character is argued. The effect of nitrous, sulphurous, and sulphuric acids on emulsin was studied. Sulphurous acid was not more fatal to emulsin than sulphuric acid, although on living cells it is more so, presumably on account of its action on the aldehyde groups of the protein molecule. From this, the absence of aldehyde groups from enzymes is argued.

Working on yeast, it was found possible to kill yeast-cells by means of sulphuric acid, formaldehyde, and mercuric chloride without inhibiting the activity of zymase. Dextrose, although directly fermentable, does not ferment more rapidly than sucrose or maltose. It is suggested that monose sugars obtained by the resolution of the higher sugars are more rapidly attacked by zymase when in the nascent state. G. W. R.

Production of Compounds containing Arsenic as a Centre of Optical Activity. GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1921, **119**, 426—437).

Indirect Reduction of 3-Amino-4-hydroxyphenylarsinic Acid to Salvarsan. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 370—375. Compare this vol., i, 70).—3-Amino-4-hydroxyphenylarsinic acid is reduced in hydrochloric acid solution to 3-amino-4-hydroxyphenylarsenious oxide hydrochloride by means of hydriodic acid and sulphur dioxide. The excess of sulphur dioxide is removed by aeration, and the liquid further reduced by hypophosphorous acid (*loc. cit.*), the salvarsan being precipitated as its dihydrochloride by pouring the liquid into hydrochloric acid diluted with an equal volume of water. This product is readily soluble in water and of low toxicity.

If the solution from the first reduction is boiled, instead of aerated as above, to expel the sulphur dioxide and then reduced with hypophosphorous acid, the product is salvarsan polyarsenide. When 3-amino-4-hydroxyphenylarsenious oxide is boiled in hydrochloric acid, *o*-aminophenol is the final product, an intermediate product being 3 : 3′-diamino-4 : 4′-dihydroxydiphenylarsenious oxide. W. G.

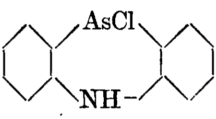
Arsenical Compounds Related to Salvarsan. GEORGE W. RAIZISS and JOSEPH L. GAVRON (*J. Amer. Chem. Soc.*, 1921, **43**, 582—585).—An account of the preparation and properties of compounds closely related to arsphenamine (salvarsan), which possibly may be present in it as impurities and give rise to the undesirable symptoms which sometimes follow its administration. 3-*Acetylamino*-4-*hydroxyphenylarsinic acid*, $C_8H_{10}O_5NAs$, gives 3 : 3′-*diacetylamino*-4 : 4′-*dihydroxyarsenobenzene*, $C_{16}H_{16}N_2O_4As_2$, on reduction. Similarly, 3 : 5-*diacetylamino*-4-*hydroxyphenylarsinic acid*, $C_{10}H_{13}N_2O_6As$, gives 3 : 3′ : 5 : 5′-*tetracetylamino*-4 : 4′-*dihydroxyarsenobenzene*, $C_{20}H_{22}O_6N_4As_2$. 3 : 5 : 3′ : 5′-Tetramino-4 4′-dihydroxyarsenobenzene tetrahydrochloride exists in two forms, one easily soluble, the other sparingly so, in methyl alcohol. The stabilities of phenylarsinic acids and arsenobenzenes diminish, and the solubilities of the corresponding hydrochlorides increase, with the number of amino-groups introduced. J. K.

Halogen United to Ring Carbon and its Replacement by Other Substituents. III. Preparation of Arsinic and Sulphonic Acids. KARL W. ROSENMUND (*Ber.*, 1921, **54**, [*B*], 438—440. Compare A., 1920, i, 44; this vol., i, 103).—Phenylarsinic acid is obtained in small yield when bromobenzene, normal potassium arsenite, water, and copper sulphate are heated at 180—200°. Similarly, potassium *o*-bromobenzoate potassium arsenite, copper powder, and aqueous alcohol at about 90° give *o*-carboxyphenylarsinic acid, $CO_2H\cdot C_6H_4\cdot AsO(OH)_2$.

[With E. STRUCK.]—Benzenesulphonic acid is prepared from

bromobenzene, sodium sulphite, and copper sulphate in the presence of water at 180° and subsequently at 200°. Similarly *p*-bromotoluene gives toluene-*p*-sulphonic acid. Sodium *o*-bromobenzoate and sodium sulphite, in like manner, yield *o*-sulphobenzoic acid at 120—130° or when boiled under reflux. *m*-Sulphobenzoic acid is prepared from *m*-bromobenzoic acid at 170—180°. H. W.

Cyclic Arsenic Compounds of the Aromatic Series. HEINRICH WIELAND and WILHELM RHEINHEIMER (*Annalen*, 1921, **423**, 1—38).—Phenarsazine chloride (annexed formula), prepared by



the action of arsenic trichloride on diphenylamine, exhibits marked chemical similarity to diphenylarsenious chloride, from which it differs only by the NH– bridge. By alkalis, it is converted into the corresponding oxide, $\left(NH<\frac{C_6H_4}{C_6H_4}>As\right)_2O$, and by sodium methoxide into the methyl ether, $NH\colon(C_6H_4)_2\colon As\cdot OMe$; the acetate and sulphide may be obtained by treating the oxide with acetic acid and hydrogen sulphide respectively. All these compounds give phenarsazine chloride again when treated with hydrochloric acid. By the action of mild oxidising agents, such as hydrogen peroxide in glacial acetic acid, phenarsazine chloride and its derivatives with tervalent arsenic yield phenarsazinic acid, $NH\colon(C_6H_4)_2\colon AsO\cdot OH$. With the exception of the sulphide, the above derivatives are colourless, but the chloride itself is intensely yellow. The properties of the chloride are, however, those, not of a quinonoid salt-like compound, but of an arsine chloride; thus, as dust or vapour, the compound exhibits the irritating effect of diphenylarsenious chloride. *N*-Methylphenarsazine chloride, obtained in very small yield from diphenylmethylamine and arsenic trichloride, is also intensely yellow, the colour being regarded as due to intramolecular reciprocal influence between the AsCl– and NH– groups.

The chloride does not lose hydrogen chloride when treated with either pyridine or dimethylamine, but sublimation in a vacuum of the amino-derivative or of the oxide, or removal of the elements of methyl alcohol from the methyl ether (see above) by passage of dry carbon dioxide through its diphenylmethylamine solution, yields phenarsazine, $C_6H_4<\!\!\!<\frac{As}{N}\!\!>C_6H_4$, which is an orange-yellow compound and forms solutions which become decolorised almost immediately in the air; towards oxygen phenarsazine is stable, the decolorisation being effected by atmospheric moisture, which brings about conversion into the oxide, $[NH\colon(C_6H_4)_2\colon As]_2O$. Phenylarsazine is a highly reactive compound and unites with great rapidity with 1 mol. of an alcohol, phenol, acetic acid, amine, or hydrogen chloride, the reactions, excepting that with hydrogen chloride, being reversible, so that, when the colourless solution of one of the compounds in an indifferent solvent of high boiling point is heated it becomes intensely orange-yellow, whilst when shaken at a lower temperature in contact with moist air it undergoes almost instant

decolorisation. The readiness with which phenarsazine forms additive compounds is regarded as a consequence of the slight tendency of arsenic to form part of a quinonoid system, this acting against the formation of a double linking between arsenic and carbon; arsenomethines with the group ·As:C· in place of the group ·N:C of the azomethines are as yet unknown.

Careful treatment of phenarsazine chloride in acetic acid with fuming nitric acid yields *o*- and especially *p*-nitrophenarsazine chlorides, together with the *pp'*-dinitro-compound; oxidation of these products by means of hydrogen peroxide yields the corresponding nitrophenarsazinic acids, which are obtainable also by nitration of phenarsazinic acid, the ortho-derivative being formed in the larger proportion.

p-Nitrophenarsazinic acid forms two series of salts: (1) monobasic, yellow salts, which are simple arsenates, and (2) cherry-red, dibasic salts with a bronze-like lustre; these are undoubtedly quinonoid and must be regarded as aci-nitro-salts,

$$C_6H_4{<}\underset{\text{-----------N}}{\overset{AsO(ONa)}{}}{>}C_6H_3{:}NO{\cdot}ONa.$$

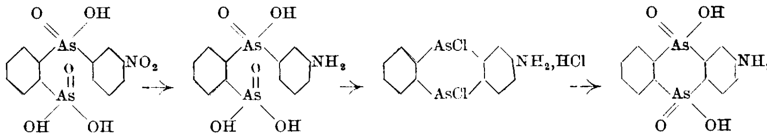
Fresh support is thus furnished for the view that *p*-nitrodiphenylamine derivatives are capable of forming quinonoid salts (compare Wieland and Roth, A., 1920, i, 304). *o*-Nitrophenarsazinic acid forms no quinonoid salts.

By means of ferrous hydroxide the nitro-acids may be converted into the corresponding amino-acids, the quinquevalent arsenic remaining almost completely intact. The amino-acids are colourless, crystalline compounds of amphoteric character and may be readily isolated by means of their hydrochlorides. Like *p*-aminodiphenylamine, *p*-aminophenarsazinic acid yields a sparingly soluble emeraldin-like colouring matter when oxidised in acid solution; in aqueous solution its sodium salt is oxidised by silver oxide to the simple quinonedi-imine.

m-Aminophenarsazinic acid has been prepared synthetically by heating *m*-aminodiphenylamine with arsenic trichloride and oxidising the resulting chloride by means of hydrogen peroxide. Contrary to what might be expected, the para-relationship of the amino-group to the tervalent arsenic causes no tendency towards the formation of a quinonoid oxidation product.

Various attempts to nitrate arsanthrene dichloride (compare Kalb, succeeding abstract), carried out with the view of obtaining nitro- and hence amino-derivatives of arsanthrene, resulted in the preparation of the stable arsanthrenic (*o*-diphenylenediarsinic) acid, which resists the action of the most energetic nitrating agents. Phenylarsinophenyl-*o*-arsinic acid (compare Kalb, *loc. cit.*) is, however, comparatively readily nitrated, since one of the rings carries only one of the arsinic groups, to which the difficulty of substitution is due. The nitro-acid is readily reduced by means of ferrous hydroxide to the amino-acid, and in the latter the two arsenic atoms are reduced by sulphur dioxide in concentrated hydrochloric acid to the tervalent chloride condition, the para-amino-group then causing closure of the ring with elimination of

hydrogen chloride. Oxidation of the aminoarsanthrene dichloride then yields aminoarsanthrenic acid :



m : *m*-Diaminodiphenylarsinic acid may be obtained by gentle reduction of the corresponding dinitro-acid; the isomeric *p*-acid is already known.

Phenarsazine chloride, m. p. 193°, may be sublimed in a vacuum and dissolves in concentrated sulphuric acid to a deep red solution.

The *oxide*, $C_{24}H_{18}ON_2As_2$, crystallises in colourless leaflets, m. p. above 350°, is stable towards alkalis, even in the hot, and forms ethers with alcohols and with phenol. The *methyl ether*, $C_{13}H_{12}ONAs$, crystallises in long, colourless needles, m. p. 194°; the *acetate*, $NH(C_6H_4)_2As{\cdot}OAc$, green, glistening leaflets, m. p. 223—224°, and the *sulphide*, $C_{24}H_{18}N_2SAs_2$, slender, felted needles or leaflets, m. p. 262°.

Triphenarsazine chloride,

$$NH\colon(C_6H_4)\colon_2As{\cdot}N\colon(C_6H_4)_2\colon As{\cdot}N\colon(C_6H_4)_2\colon AsCl,$$

obtained when phenarsazine chloride is boiled with dry pyridine, quinoline, or dimethylaniline, forms orange-yellow crystals, m. p. 260—263°, and is converted into phenarsazine oxide on prolonged boiling with a fresh quantity of the base.

Triphenarsazinamine, $(NH\colon(C_6H_4)_2\colon As)_3N$, formed when dry ammonia is passed into a boiling xylene solution of phenarsazine chloride, is a colourless compound, m. p. 295—300° (frothing), which loses ammonia and yields phenarsazine acetate when dissolved in glacial acetic acid.

Phenarsazine, $C_{12}H_8NAs$, m. p. about 310°, like all its derivatives, dissolves in concentrated sulphuric acid, giving a carmine-red solution, from which the orange-yellow sulphate is separated on addition of water.

N-*Methylphenarsazine chloride*, $C_6H_4<^{AsCl}_{NMe}>C_6H_4$, forms yellowish-green needles, m. p. 203°, dissolves in concentrated sulphuric acid without characteristic coloration, and first gives a blue coloration and then undergoes nitration when treated with concentrated nitric acid; the *N*-methyldinitro-acid does not form deeply coloured alkali salts.

pp′(?)-*Dinitrophenarsazine chloride*, $C_{12}H_7O_4N_3ClAs$, forms pale yellow needles, m. p. far above 300°.

o-*Nitrophenarsazine chloride*, $C_{12}H_8O_2N_2ClAs$, crystallises in scarlet needles, m. p. 156°, and the p-*isomeride* in dark greenish-yellow leaflets, mostly united to nodules.

Phenarsazinic acid, $C_{12}H_{10}O_2NAs$, crystallises in colourless felted needles, m. p. above 300°.

o-*Nitrophenarsazinic acid*, $C_{12}H_9O_4N_2As + H_2O$ (or $+ H_4C_2O_2$), forms bright yellow needles of high melting point. The p-*isomeride* was also analysed. pp′-*Dinitrophenarsazinic acid*, $C_{12}H_8O_6N_3As$, crystallises in bright yellow needles.

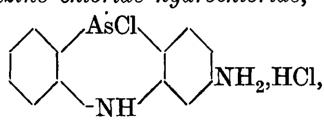
o-*Aminophenarsazinic acid*, $C_{12}H_{11}O_2N_2As$, forms colourless needles or pink leaflets (+ Et·OH), has no sharp melting point, and, unlike the para-acid, is not auto-oxidisable. The p-*isomeride*, when oxidised in acid solution, exhibits colour changes similar to those occurring with *p*-aminodiphenylamine.

p-*Aminophenarsazine chloride* was obtained as *hydrochloride*, $C_{12}H_{11}N_2Cl_2As$, which crystallises in yellowish-green leaflets and, even in traces, exerts an intensely irritant action on the mucous membranes of the eyes, nose, and throat.

pp′-*Diaminophenarsazinic acid*, $C_{12}H_{12}O_2N_3As$, is characterised by the intense coloration produced when aqueous solutions of its alkali salts are shaken with silver oxide; its *hydrochloride*, (2HCl), was analysed.

m-*Aminodiphenylamine*, $C_{12}H_{12}N_2$, prepared by reducing the corresponding nitro-compound by means of tin and hydrochloric acid, crystallises in stellar aggregates of long, colourless leaflets, m. p. 76—77°. It forms mono- and di-acid salts and may be diazotised in the usual way, a brick-red colouring matter being obtained by coupling the diazo-solution with β-naphthol.

m-*Aminophenarsazine chloride hydrochloride*,



forms yellowish-green leaflets; m-*aminophenarsazinic acid*, $C_{12}H_{11}O_2N_2As_2$, prisms with a rhombic section, and its *hydrochloride*, colourless prisms.

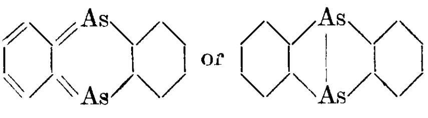
Arsanthrenic (*diphenylene*-o-*diarsinic*) *acid*, $C_6H_4<\substack{AsO(OH)\\AsO(OH)}>C_6H_4$, forms long, colourless prisms, m. p. above 360°.

m - *Nitrophenylarsinophenyl* - o - *arsinic acid*, forms colourless crystals, and the corresponding *amino*-acid, $C_{12}H_{13}O_5NAs_2$, stellar aggregates of pink needles. m-*Aminoarsanthrene dichloride hydrochloride* forms colourless crystals, and *aminoarsanthrenic acid*, $C_{12}H_{11}O_4NAs$, colourless needles.

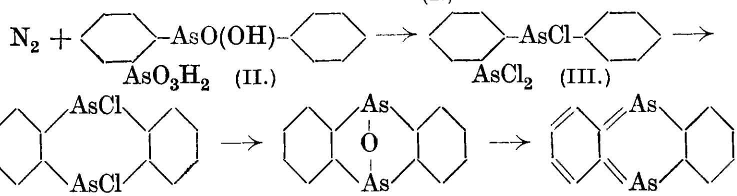
m : *m*′-Dinitrodiphenylarsinic acid is not obtainable by the method given by Michaelis (A., 1902, i, 515), but conditions have been established which furnish an almost quantitative yield. m : m′-*Diaminodiphenylarsinic* acid, $AsO(C_6H_4{\cdot}NO_2)_2{\cdot}OH$, is obtained by reducing the dinitro-acid by means of ferrous hydroxide. If the reduction is effected by means of powdered iron, very little diamino-acid is obtained, the principal product consisting of the oxide, $[(NH_2{\cdot}C_6H_4)_2As]_2O$, which is converted by concentrated hydrochloric acid into the corresponding *arsine chloride dihydrochloride*, $C_{12}H_{12}N_2ClAs,2HCl$, this exhibiting the irritating action of arsine chlorides.

T. H. P.

Arsanthrene (Diphenylenediarsine). LUDWIG KALB (*Annalen*, 1921, **423**, 39—75).—The author has effected the synthesis of diphenylenediarsine (annexed formula),



to which he gives the name arsanthrene, in accordance with the following scheme, the starting point being *o*-nitroaniline: $NO_2{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow NO_2{\cdot}C_6H_4{\cdot}AsO_3H_2 \longrightarrow NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2 \longrightarrow \underset{(I.)}{OH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}AsO_3H_2} + Ph{\cdot}As{:}O =$



(IV.) (V.) (VI.)

Phenylarsinophenyl-*o*-arsinic acid (II) is accompanied by various impurities, including azobenzene-*o* : *o'*-diarsinic acid,

$$H_2O_3As{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}AsO_3H_2,$$

which it is difficult, although necessary, to remove. Compound II may also be obtained, although in poor yield, as follows:

$$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OH + Ph{\cdot}As{:}O \longrightarrow \underset{(VII.)}{NO_2{\cdot}C_6H_4{\cdot}AsOPh{\cdot}OH} \longrightarrow$$

$$\underset{(VIII.)}{NH_2{\cdot}C_6H_4{\cdot}AsOPh{\cdot}OH} \longrightarrow H_2O_3As{\cdot}C_6H_4{\cdot}AsOPh{\cdot}OH.$$

Conversion of the diazo-compound of *o*-aminodiphenylarsinic acid (VIII) into phenylarsinophenyl-*o*-arsinic acid (II) is accompanied by the formation of a considerable proportion of a deep, brownish-red azoarsinic acid, probably $(OH{\cdot}AsPhO{\cdot}C_6H_4{\cdot}N{:})_2$.

Since *o*-benzoylbenzoic acid readily undergoes ring-closure to anthraquinone, it seemed possible that treatment of compound II with condensing agents might lead to the formation of arsanthrenic acid $\overset{OH}{\underset{O}{}}\!\!>\!As\!<\!\overset{C_6H_4}{\underset{C_6H_4}{}}\!\!>\!As\!<\!\overset{OH}{\underset{O}{}}$, but the compound undergoes no change when heated with concentrated sulphuric acid at 150°. Arsanthrenic acid may, however, be prepared by oxidising arsanthrene or its arsenic derivatives by means of nitric acid (compare Wieland and Rheinheimer, preceding abstract).

Treatment of a concentrated hydrochloric acid solution of phenylarsinophenyl-*o*-arsinic acid with sulphur dioxide in presence of hydriodic acid yields, besides phenylchloroarsinophenyl-*o*-arsine dichloride, also phenylarsine dichloride and diphenylenediarsine dichloride (arsanthrene chloride) (IV). As is commonly the case with halogenated derivatives of arsines, the chlorine in arsanthrene chloride is readily hydrolysable, the action of sodium carbonate solution yielding, not the dihydroxy-compound, but arsanthrene oxide (V). Arsanthrene (VI) is readily obtained from the chloride or oxide by treatment with reducing agents; it is an orange-yellow

compound, although the analogous nitrogen compound, phenazine, is only pale yellow. The fact that arsanthrene oxide is colourless, whilst phenazine oxide is yellow to red, is regarded as due to the presence of the oxygen-bridge in the former, the latter being assumed to have the unsymmetrical quinonoid structure, $C_6H_4{<}{\overset{NO}{\underset{N-}{}}}{>}C_6H_4$.

o-*Nitrophenylarsine dichloride*, $NO_2{\cdot}C_6H_4{\cdot}AsCl_2$, crystallises in pale yellow prisms, m. p. 49—50°.

Phenylarsinophenyl-o-*arsinic acid* (II) crystallises in microscopic, long, quadrilateral leaflets, m. p. 350° (decomp.) or 360° (rapid heating). *Azobenzene*-o : o′-*diarsinic acid*, $C_{12}H_{12}O_6N_2As_2$, forms orange-yellow needles, m. p. 272°; o-*nitrodiphenylarsinic acid* (VII), microscopic, oblique, quadrilateral pillars or rhombohedra, m. p. 197—198°, and o-*aminodiphenylarsinic acid* (VIII), a snow-white, crystalline powder, m. p. 129—130°, becoming clear at 135°.

Arsanthrene chloride (IV) forms large, lanceolate crystals, m. p. 182—183°; *phenylchloroarsinophenyl*-o-*arsine dichloride* (III), nodular aggregates of slender, white needles, m. p. 153—155°; *arsanthrene oxide* (V), quadrilateral leaflets or bundles of needles, m. p. 196°; and *arsanthrene* (VI), orange-yellow, rhomboidal plates, turning orange-red at about 170°, greenish-yellow at 290°, m. p. 340°.

In view of the formation of triphenylarsine from chloro- or bromo-benzene, arsenic trichloride and sodium in ethereal solution (Michaelis and Reese, A., 1883, 327; Philips, A., 1886, 618; Michaelis and Loesner, A., 1894, i, 187; Michaelis, A., 1902, i, 515), it seemed possible that arsanthrene chloride might be obtainable by the condensation, in presence of sodium, of either (1) *o*-dibromobenzene and arsenic trichloride, or (2) 2 mols. of *o*-bromophenylarsine dichloride. In neither case was the expected result obtained, the ortho-bromine atom apparently exerting steric hindrance. The *o*-bromophenylarsine dichloride was obtained from *o*-bromoaniline by way of *o*-bromophenylarsinic acid.

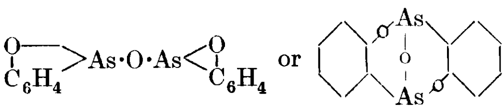
o-Diazophenylarsine oxide is highly unstable and decomposes, either alone or in presence of alkali, yielding *o*-hydroxyphenylarsine oxide anhydride, which is readily hydrolysed and dissolved by dilute sodium hydroxide solution and is converted into *o*-hydroxyphenylarsine dichloride by treatment with hydrochloric acid. The above oxide anhydride is better obtained by diazotising *o*-arsanilic acid and reducing the diazo-compound by means of aqueous sulphur dioxide, the intermediate diazophenylarsine oxide decomposing in a few moments to the anhydride; the latter may be prepared also by the action of sodium hydrogen sulphite solution on *o*-hydroxyphenylarsinic acid, which may be obtained by boiling *o*-diazophenylarsinic acid solution (Jacobs and Heidelberger, A., 1919, i, 604).

Treatment of *o*-phenylenediarsinic acid with hydrogen chloride and sulphur dioxide in presence of hydriodic acid yields, not *o*-phenylenediarsine tetrachloride, but *o*-phenylenediarsine oxychloride, $C_6H_4{<}{\substack{AsCl\\AsCl}}{>}O$. *o*-Phenylenediarsinic acid, prepared by diazotising *o*-arsanilic acid and treating the product with sodium arsenite, is a strong acid, sparingly soluble in water.

o-*Bromophenylarsinic acid*, $C_6H_4Br{\cdot}AsO_3H_2$, crystallises in white leaflets, and o-*bromophenylarsine dichloride*, $C_6H_4Br{\cdot}AsCl_2$, in stout, colourless plates, m. p. 63°.

o-*Aminophenylarsine oxide*, $NH_2{\cdot}C_6H_4{\cdot}AsO$, forms a white powder. which gradually becomes blue.

o-*Hydroxyphenylarsine oxide anhydride* (annexed formulæ) forms colourless, granular crystals, m. p. 177°, and in the form of powder produces intense irritation of the mucous membranes.



o-*Hydroxyphenylarsine dichloride*, $OH{\cdot}C_6H_4{\cdot}AsCl_2$, forms flat, pale yellow, lanceolate crystals, m. p. 81—82°.

o-*Phenylenediarsinic acid*, $C_6H_4(AsO_3H_2)_2$, forms white, microscopic needles (+ H_2O) and does not melt at 360°; o-*phenylenediarsine oxychloride*, $C_6H_4OCl_2As_2$, crystallises in almost colourless, quadrilateral plates, m. p. 148°. T. H. P.

Mercuri-organic Derivatives. II. Nitrobenzene Mercury Compounds; An Indirect Method of Mercurising Organic Compounds. MORRIS S. KHARASCH and LYMAN CHALKLEY, JUN. (*J. Amer. Chem. Soc.*, 1921, **43**, 607—612).—o-*Nitrophenylmercurichloride*, $NO_2{\cdot}C_6H_4{\cdot}HgCl$, faintly yellow crystals, m. p. 185° (corr.), is prepared from *o*-nitrobenzenesulphinic acid and mercuric chloride (compare Peters, A., 1905, i, 640); the meta-*isomeride*, white crystals, m. p. 236—237° (corr.), and the para-*isomeride*, colourless crystals, m. p. 265—266° (corr., decomp.), are similarly prepared. They give nitrobenzene on treatment with hydrochloric acid, and the corresponding bromonitrobenzenes by the action of a solution of bromine in potassium bromide solution. The last reaction confirms the validity of Dimroth's analogous method of determining the orientation of such mercury compounds (A., 1902, i, 656). Sodium nitrite is not produced when *o*-nitrophenylmercurichloride is boiled with sodium hydroxide. These results, with the formation of benzene by the action of hydrochloric acid on *p*-phenylenedimercuriacetate (Dimroth, A., 1899, i, 428), and the mercurisation of picric acid (Hantzsch and Auld, A., 1905, i, 742), are considered to require modification of Fry's electronic formula for benzene (A., 1915, i, 391). J. K.

Reaction of Alkali Haloids with Mercury Derivatives of Phenol. F. C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1921, **43**, 619—624).—A number of instances are quoted from the literature in which organic mercuri-derivatives, including those of the naphthols (Brieger and Schulemann, A., 1914, i, 611) suffer rupture of the C·Hg linking on treatment with potassium haloids. Improved conditions are given for the preparation of *o*- and *p*-hydroxyphenylmercurichlorides. These, as well as the dimercuri-derivative simultaneously produced, react almost quantitatively with potassium iodide, slightly with the bromide, and not at all with the chloride, to give phenol, and

potassium hydroxide, with potassium mercuriodide and potassium chloride. The corresponding acetyl derivatives do not undergo this reaction, but with sodium thiosulphate give the mercury bisphenylacetates, which are quantitatively reconverted into the original derivatives by mercuric chloride. *Mercury bis*-2 : 2′-*phenylacetate*, $C_{16}H_{14}O_4Hg$, needles, m. p. 125°, gave bishydroxyphenylmercuric oxide (Dimroth, A., 1902, i, 656), by treatment successively with boiling sodium hydroxide and acetic acid; and the para-*isomeride*, white crystals, m. p. 172—173°, behaved similarly. This reaction apparently constitutes a new method of breaking down the ·Hg·C⫶ linking. J. K.

Compounds of Antipyrine with Mercury. E. Oliveri-Mandalà (*Gazzetta*, 1921, **51**, i, 125—130).—With haloid salts of mercury, antipyrine forms compounds of the two types, $C_{11}H_{12}ON_2,HgR_2$ and $(C_{11}H_{12}ON_2)_2HgR_2$, which do not give the reactions characteristic of mercury and are regarded as having the constitutions, $\boxed{}\!>$NMeR·HgR and $\left(\boxed{}\!>\text{NMeR}\right)_2$Hg. The author finds that antipyrine readily combines with unstable mercuric compounds, such as HgCl·OH, HgI·OH, and $HgCl·NH_2$. On the assumption made by Knorr that antipyrine behaves as an unsaturated compound, $\begin{matrix}-\text{CO}-\text{NPh}\\ \text{||}\qquad\quad\\ \text{CH}-\text{CMe}\end{matrix}\!\!>\!\text{NMe}-$, and that the negative portion of the added molecule unites with the nitrogen atom carrying the methyl group, the author's compounds would have such formulæ as ${}^{\text{HgCl}}\boxed{}\!>$NMe·OH, rather than $\boxed{}\!>$NMe(HgCl)·OH.

Pyramidone combines with mercuric chloride, giving a compound of the same type as that obtained from antipyrine, but it does not unite with either $Hg(OH)_2$, or HgCl·OH, or $HgCl·NH_2$, under conditions sufficing to bring about the union with antipyrine. The replacement of the methinic hydrogen of the antipyrine molecule by the dimethylamino-group present in pyramidone evidently destroys the mobility of arrangement of the valencies of the nucleus.

The *compound* $C_{11}H_{12}ON_2,HgCl·NH_2$ forms crystals; the *compound* $C_{11}H_{12}ON_2$,HgCl·OH or ${}^{\text{HgCl}}\boxed{}\!>$$NMe·NH_2$, crystals, m. p. 93° (compare Paderi, A., 1920, i, 94), and the *compound* $C_{11}H_{12}ON_2$,HgI·OH shining, yellow scales, m. p. 135°.

T. H. P.

Physiological Chemistry.

Alveolar Tension of Carbon Dioxide in the Lungs. Its Importance for the Regulation of Breathing and for the Estimation of Acidosis in Diabetes mellitus. L. FARMER LOEB (*Zeitsch. ges. expt. Med.*, 1920, ii, 16—39; from *Chem. Zentr.*, 1921, i, 504).—Zuntz's method (which has not been published

previously) for the measurement of alveolar carbon dioxide tension differs from that of Haldane in that the last fractions of expired air from a large number of respirations are collected and mixed; a full description of the procedure is given. The results, which agree sufficiently well with those of Haldane, are lower than the generally recorded values. In one case of diabetes with acidosis, the values were normal, whilst in a second case they were higher.

H. W.

Effect of Temperature on the Reaction of Blood. JOSÉ MARIA DE CORRAL (*Anal. Fís. Quím.*, 1920, **18**, 109—118).—A discussion of the influence of temperature on the hydrogen- and hydroxyl-ion concentrations of blood and serum. Attention is directed to the effect of equilibration with carbon dioxide. The P_H of blood is not affected by changes of temperature provided the blood is equilibrated with carbon dioxide. G. W. R.

Chemical Changes in the Blood after Pyloric Obstruction in Dogs. A. B. HASTINGS, C. D. MURRAY, and H. A. MURRAY, JUN. (*J. Biol. Chem.*, 1921, **46**, 223—232).—In order to produce, if possible, the symptoms of gastric tetany, the pylorus was closed in eight dogs. The operation was followed by marked increase in the carbon dioxide-combining power of the blood (50—100% or more), a striking fall in the chlorine-ion concentration (to half or less), and a slight increase in the calcium content of the serum.

G. B.

Alkali Reserve of the Blood of Lower Vertebrates. J. B. COLLIP (*J. Biol. Chem.*, 1921, **46**, 57—59).—There is a great specific and individual variation and an acid-base transfer between cells and plasma in the blood of birds, turtles, and frogs examined. G. B.

The Blood of the Silk-worm. SÔJIRÔ KAWASE, KEIJI SUDA, and KAKUJI SAITÔ (*J. Chem. Soc. Japan*, 1921, **42**, 118—130).—The blood of the silk-worm larva is amphoteric to litmus paper, whilst that of the pupa is alkaline. In both fluids, D^{17} 1·029. It acquires a black tinge when set aside for a few days, but does not coagulate. It contains amino-acids (ninhydrin reaction) and proteins (principally albumin), but not reducing sugar, ammonium salts, carbamide, or uric acid. It also contains oxydase, tyrosinase, trypsin, diastase, and invertase. K. K.

The Acid-base Exchange between the Plasma and the Red Blood Cells. J. B. COLLIP (*J. Biol. Chem.*, 1921, **46**, 61—72).—The carbon dioxide-combining power of blood from a considerable number of animals, treated in a variety of ways, was determined by van Slyke's method. By changing the pressure of the carbon dioxide with which the blood is brought into equilibrium, a considerable acid-base transfer between cells and plasma may occur, in agreement with the results of van Slyke and Cullen (A., 1917, i, 521), Joffe and Poulton and Campbell and Poulton (this vol., i, 141). The author has also used Mellanby and Thomas's ashing method (this vol., i, 142) but does not agree with all their conclusions. Part of the alkali of the blood is bound by an organic substance

(probably protein), and the bicarbonate rather than the proteins is the vehicle transporting carbon dioxide in the body. G. B.

The Partition of Phosphates between Blood Corpuscles and Plasma in Vivo and in Vitro. POUL IVERSEN (*Biochem. Zeitsch.*, 1921, **114**, 297—309).—On the addition of a solution of disodium hydrogen phosphate to defibrinated rabbit blood a certain number of phosphate ions enter the blood corpuscles in the course of the first two hours, after which time the diffusion ceases. The increase in the acid soluble phosphate brought about by the addition of the salt is more marked in the serum than in the corpuscles. When disodium hydrogen phosphate is injected intravenously in a nephrectomised rabbit, the concentration of the "acid soluble phosphate" in the plasma slowly decreases after the injection, whilst that of the corpuscles accordingly increases. S. S. Z.

Detection of Albumoses in Blood Plasma, Serous Solutions, and Exudates. CH. ACHARD and E. FEUILLIÉ (*Compt. rend. Soc. Biol.*, 1920, **83**, 1535—1539; from *Chem. Zentr.*, 1921, i, 385).—Normal serum contains, for a considerable time after the intake of food, 0·03 to 0·4% albumoses, according to the method used for the removal of proteins. After a heavy meat meal the albumose content of arterial blood rises markedly. Higher values than those to be expected from the food taken are found in febrile conditions and in albuminuria. In syphilitic sera giving positive Bordet-Wassermann tests, the content of albumose was raised. Many pathological sera giving a negative Wassermann test, however, show a high albumose content.

The albumose content of blood serum was lowered in four cases of icterus. The presence of albumoses was established in certain pathological exudates. G. W. R.

Albumoses of the Cells and Tissues. CH. ACHARD and E. FEUILLIÉ (*Compt. rend. Soc. Biol.*, 1920, **83**, 1584—1587; from *Chem. Zentr.*, 1921, i, 541).—Two grams of albumoses are found to be present in a litre of the red blood corpuscle pulp obtained by centrifuging three times and washing. The corresponding amount of blood contains only 0·3—0·4 gram. The difference cannot be explained solely by the adsorption of albumoses from the excess of plasma by the precipitated albumin; it appears more probable that a compound is formed between the albumoses of the corpuscles and the lipoids of the plasma. White blood corpuscles contain 1·5 grams of albumoses in the litre. Plasma rich in globulin yields more albumoses than ordinary plasma. Differing quantities of albumoses were found in the various tissues, the relationships resembling those found for the lipoids by Mayer and Schaeffer (lungs, 14·4, kidneys, 9·4, liver and brain, 8, red muscle, 4·4, pale muscle, 3 grams per kilo). H. W.

Fibrin Clotting. II. The Combined Chlorine in the Blood. W. FALTA and M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1921, **114**, 310—317).—The chlorine content of plasma and other

serous body fluids, serum excepted, when estimated by incineration, is higher than when estimated by precipitation. This difference in the combined chlorine is due to the condition of dispersion of the respective liquids and is not always proportional to the concentration of the protein. S. S. Z.

The Relation of Pressure and Temperature to Enzyme Action. The Influence of Pressure on the Velocity of Peptic, Tryptic, and Diastatic Hydrolysis. SIGMUND FRÄNKEL and GINO MELDOLESI (*Biochem. Zeitsch.*, 1921, **115**, 85—95).—During the first two hours of peptic digestion there is more protein hydrolysed when the pressure is high than when the digestion is carried out under ordinary pressure. The digestion under pressures higher than five atmospheres shows a lower acceleration than under a pressure of five atmospheres. The acceleration in the velocity of hydrolysis during the first two hours effected by high pressure diminishes eventually. In the case of trypsin the increase in the rate of digestion is more regular. Diastatic hydrolysis is accelerated by increased pressure during the first two hours, after which time it becomes slower and remains constant. S. S. Z.

The Digestive Enzymes of the Silk-worm. SÔJIRÔ KAWASE, KEIJI SUDA, and KAKUJI SAITÔ (*J. Chem. Soc. Japan*, 1921, **42**, 103—117).—The work was done on the gastric juice, and the stomach walls (and the glycerol extract of the latter) of the silk-worm. The proteolytic enzyme present is trypsin. The sucroclastic enzyme is amylopsin, which acts on starch in neutral and alkaline solutions, producing maltose and achroodextrin, whilst invertase is an endo-enzyme, acting in neutral and alkaline solutions. The action of the lipolytic enzyme, lipase, is weak for the higher fats, such as olive oil, and for ethyl acetate. Oxydase, peroxydase, and tyrosinase were not present in the gastric juice. K. K.

Magnesium Metabolism. Influence of Subcutaneous Injection of Magnesium Sulphate on the Elimination of Calcium in the Urine of Healthy Children and in Cases of Calcuria. ER. SCHIFF and E. STRANSKY (*Jahrb. Kinderheilk.*, 1920, [iii], **43**, 205—209; from *Chem. Zentr.*, 1921, i, 505).—Further investigations have confirmed the increase (from three to four times) in the elimination of calcium in the urine of normal children after subcutaneous injection of magnesium sulphate; this increase is comparatively little in cases of calcuria. Consideration of these and other observations renders it probable that the metabolic changes accompanying the loss of calcium are caused by an abnormal behaviour of the magnesium metabolism. H. W.

Intermediate Carbohydrate Metabolism in Man. II. Quantitative Behaviour of Formic Acid in Normal and Pathological Blood. WILHELM STEPP and HERMANN ZUMBUSCH (*Deut. Arch. Klin. Med.*, 1920, **134**, 112—118; from *Chem. Zentr.*, 1921, i, 504. Compare this vol., i, 203).—The concentration of formic acid is particularly variable under pathological conditions. In ten cases of healthy individuals, the extreme values observed

were 1·1 and 8·5 mg. in 100 c.c. of blood. Formic acid was completely absent in three cases of diabetes mellitus and, in eleven other cases, was present in less than the normal amount. Smaller values are also found with patients suffering from disease of the kidneys. The estimation is effected by Reisser's method (A., 1916, ii, 455); the addition of hydrochloric acid, however, is omitted thus avoiding a source of error. H. W.

Lecithin. III. Fatty Acids of Lecithin of the Egg Yolk. P. A. Levene and Ida P. Rolf (*J. Biol. Chem.*, 1921, **46**, 193—207. Compare A., 1920, i, 788).—Methods are given for obtaining lecithin cadmium chloride free from fats, cerebrosides, and saturated lipoids, and with a minimum content of amino-nitrogen. On hydrolysis, about half the fatty acid was found to be oleic, the other half a mixture of palmitic and stearic. These facts suggest the existence of more than one lecithin in egg yolk. G. B.

Comparative Experiments on the Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene on Isolated Frog's Heart. Werner Kiessling (*Biochem. Zeitsch.*, 1921, **114**, 292—296).—With the exception of hexachloroethane and tetrachloroethylene, the chlorine derivatives of ethane, methane, and ethylene in aqueous solution bring the ventricle in the frog's heart to a standstill. S. S. Z.

The Formation of Carbamide in the Liver after Death. R. Fosse and (Mlle) N. Rouchelman (*Compt. rend.*, 1921, **172**, 771—772).—During the aseptic autolysis of fresh liver at the ordinary temperature or at 37—40° there is marked production of carbamide. This does not occur if the liver is first plunged into boiling water for twenty minutes. W. G.

Synthesis of Hippuric Acid in the Rabbit after Exclusion of Bile from the Intestine. Howard B. Lewis (*J. Biol. Chem.*, 1921, **46**, 73—75).—Glycocholic acid is not the only, or even the principal, source of the glycine of hippuric acid. G. B.

The Causes of the Variation of the Zinc Content of Vertebrate Animals: Influence of Age. Gabriel Bertrand and R. Vladesco (*Compt. rend.*, 1921, **172**, 768—770. Compare A., 1920, i, 909).—Analyses of the whole bodies of mice, rabbits, guinea-pigs, fowls, herrings, tench, and *Idus orfus* show that in several species the zinc content is at a maximum in the young animal, although in some species there is only very slight variation with age. W. G.

The Fixation of Calcium by Animal Tissues. II. E. Freudenberg and P. György (*Biochem. Zeitsch.*, 1921, **115**, 96—108).—Calf's cartilage and cartilage from adult human beings are capable of fixing calcium independently of the anion with which it is associated. The cartilage of sucklings and fœtuses, on the other hand, cannot fix calcium out of solutions of calcium acetate and calcium nitrate. Cartilage can also fix other bi- and tervalent kations. When a solution contains calcium and magnesium

ions, the cartilage fixes less of each of these ions than it would have done if only one of these were present, thus showing that there is a mutual displacement. Calcium, however, displaces magnesium more readily than magnesium does calcium. Brain tissue fixes magnesium more readily than calcium, yet the latter displaces magnesium from it. Calcium displaces sodium from gelatin; aluminium hinders this displacement. S. S. Z.

Acidity of Goat's Milk in Terms of Hydrogen-ion Concentration, with Comparisons with that of Cow's and Human Milk. E. W. Schultz and L. R. Chandler (*J. Biol. Chem.*, 1921, **46**, 129—131).—Average goat's milk has P_H 6·53, when fresh, and 3·92 when fully soured. Van Slyke and Baker (A., 1920, i, 263) found for fresh cow's milk 6·5—7·2, usually 6·5—6·76; other authors 6·52—6·8; the maximum acidity of soured cow's milk is 4·65. Human milk has P_H between 6·86 and 7·46.

G. B.

Factors Governing the Rate of Excretion of Urea. J. Harold Austin, Edgar Stillman, and Donald D. van Slyke (*J. Biol. Chem.*, 1921, **46**, 91—112).—The authors arrive at the formula $K = D/B\sqrt{VW} = 7·5 \pm 3$ (for normal man), where D is the urea output in grams per twenty-four hours, B the blood urea in grams per litre, V the volume output in litres per twenty-four hours, W the body weight in kilos, and K the excretory constant. Ambard's first law, $D/B^2 = K$, when C, the concentration in urine, is constant (compare *Ann. Rep.*, 1916, 215—216, and 1917, 175) is shown to be a special case of the authors' formula. His second law, $D\sqrt{C} = K$, when B is constant, they consider not to hold. The main difference between the authors and Ambard is that they substitute the rate of volume output of urine for the concentration of urea in it. G. B.

Alcapton and Acetone. II. Gerhardt Katsch (*Deut. Arch. Klin. Med.*, 1920, **134**, 59—68; from *Chem. Zentr.*, 1921, i, 504—505).—It has been shown previously that elimination of homogentisic acid ceases and its place is taken by acetone in course of the hunger period in cases of alcaptonuria. A proof is thus afforded of the absence of a strict dependence of the elimination of homogentisic acid on the albumin metabolism, a possibility considered previously by Fromherz. An opportunity is thus given of testing the relationship between aromatic amino-acids and ketones. Great restriction in the albumin causes a considerable depression in the amount of homogentisic acid eliminated, but the alcaptonuria is not altered in the same manner as in the total absence of albumin. The quotient, homogentisic acid : N, remains normal (about 50) if the carbohydrate metabolism is undisturbed and ketoneuria is absent. In a further experiment, acidosis was induced by an albumin-fat diet; homogentisic acid was only found in traces and considerable quantities of acetone substances were immediately observed. On the hypothesis that a molecule of the acid corresponds with a molecule of acetone, the lack of the former is not

sufficient to enable it to be regarded as sole source of the latter. It is improbable that, in cases of limitation of carbohydrate, those substances which form alcapton are the only origins of acetone. The author is drawn to the conclusion that the hydration processes of carbohydrate and albumin are related phenomena, thus resembling those of carbohydrate and fat as observed by Embden and Isaak. H. W.

The Production and Properties of Pathological Melanin. II. The Normal Pigment of the Liver. E. SALKOWSKI (*Arch. Anat. Physiol.*, 1920, **228**, 468—475; from *Chem. Zentr.*, 1921, **1**, 541. Compare A., 1920, i, 572).—The final purification of melanin from tumours is more readily effected with alcohol containing a small amount of hydrogen chloride than with acetic acid; a specimen which had been freed completely from albumin and fat in this manner had 0·57% P. The distillate from melanin with sulphuric acid and potassium dichromate has properties similar to that derived from peptone [odour of benzaldehyde and valeraldehyde, reduction of ammoniacal silver solution in the cold, violet coloration of magenta-sulphurous acid which here persists after addition of hydrochloric acid (CH_2O)]. It also contains volatile fatty acids. Ehrlich's and Adamkiewicz's reactions give a positive result with melanin after treatment with sodium hydroxide and hydrogen peroxide, thus indicating the presence of tryptophan.

The pigment of normal liver differs entirely from pathological melanin and probably consists of two dyes which differ in their solubility in ether. H. W.

Influence of the Acid Radicle on the Anæsthetic Properties of Amino-alcohols. JOSÉ MARÍN CANO and JOSÉ RANEDO (*Anal. Fís. Quím.*, 1920, **18**, 184—206).—The anæsthetic properties of hydrochlorides of various esters of dimethylaminodimethylethylcarbinol were studied. Measuring the times required for incipient and complete anæsthesia of the sciatic nerve of frogs, comparative estimates were obtained of the anæsthetic powers of the compounds studied. The results lend support to the theory that, within limits, anæsthetic power increases with the molecular weight of the acid radicle of the ester. The esters of such dissimilar acids as benzoic, heptoic and *cyclo*hexanecarboxylic show almost equal anæsthetic powers, presumably on account of their closely approximating molecular weights. In the esters of the fatty acid series, the theory only holds for intermediated numbers. Thus, while anæsthetic power increases from the butyric ester to the undecoic ester, the palmitic ester is non-anæsthetic.

The hydrochlorides of the various esters used were prepared for the first time and their identity confirmed by analysis. G. W. R.

Anæsthetic Action of Anæsthesin [Ethyl *p*-Aminobenzoate and some of its Derivatives. J. MORGENROTH (*Ber. Deut. pharm. Ges.*, 1921, **31**, 76).—Comparative tests of the anæsthetic

action of anæsthesin and certain of its derivatives (see this vol., i, 343) were made on the cornea of the rabbit. Three minutes' treatment with anæsthesin itself rapidly produced anæsthesia lasting thirty-two minutes. Ethyl *p*-hydrazinobenzoate gave almost similar results, whilst ethyl *p*-allylthiocarbamidobenzoate had scarcely any anæsthetic action. As regards soluble compounds ethyl *p*-hydrazinobenzoate hydrochloride in 2% solution after three minutes' action produced anæsthesia lasting nine minutes. The insoluble substances act therefore more powerfully than their soluble salts. G. F. M.

Chemistry of Vegetable Physiology and Agriculture.

The Production of Volatile Fatty Acids by Bacteria of the Dysentery Group. HARPER E. ZOLLER and W. MANSFIELD CLARK (*J. Gen. Physiol.*, 1921, **3**, 325—330).—Pure cultures of the bacteria were grown in peptone solutions under aerobic and anaerobic conditions, both with and without the addition of dextrose; after a definite period the volatile fatty acids were distilled off and estimated.

Under aerobic conditions, in the presence of dextrose, formic and acetic acids were formed; in the absence of dextrose, acetic and propionic acids. Anaerobic conditions in the presence of dextrose gave formic and acetic acids; in the absence of dextrose, formic, acetic, and butyric acids, the latter in small quantity. Under similar conditions different strains produced similar amounts of acid. C. R. H.

Comparative Studies on Respiration. XIV. Antagonistic Action of Lanthanum. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, **3**, 337—342. Compare A., 1919, i, 611; 1920, i, 462, and two following abstracts).—0·000006—0·000025 molar lanthanum nitrate somewhat increases the respiration of *B. subtilis*, and higher concentrations decrease it. There is a well-marked antagonism between La-ions and Na-ions, but very little between La- and Ca-ions. 99·8 parts of sodium chloride are antagonised by 0·2 part of lanthanum nitrate. G. B.

Comparative Studies on Respiration. XV. The Effect of Bile Salts and of Saponin. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, **3**, 527—532. Compare A., 1919, i, 611; 1920, i, 462).—Sodium taurocholate increases the rate of respiration of *B. subtilis* at 0·0000125 molar concentration and decreases it at 0·001 molar and higher concentrations. This salt is antagonised by sodium chloride, most favourably by 14·375 molecular proportions of the latter. Saponin at 0·00005—0·001 molar concen-

tration decreases the rate of respiration. (For the similar antagonism of taurocholate to chloride in the case of the permeability and electric conductivity of *Laminaria*, compare Osterhout, A., 1919, i, 303). G. B.

Comparative Studies on Respiration. XVI. Hypotonic and Hypertonic Solutions. O. L. INMAN (*J. Gen. Physiol.*, 1921, **3**, 533—537).—Highly hypertonic sea-water rapidly reduces respiration of *Laminaria*, highly hypotonic solutions do the same somewhat less rapidly. Hypertonic solutions of sodium chloride, of calcium chloride, and of mixtures in the proportion 50 : 1 all lower the respiration of wheat seedlings. G. B.

Slimy Lactic Streptococcus. A Non-pathogenic Species of Lactic Ferment. H. VIOLLE (*Ann. Inst. Pasteur*, 1921, **35**, 218—229).—A lactic acid *Streptococcus* is commonly found in milk and its products which forms in sugar media a slimy substance. Its presence indicates contamination after milking by dirt or addition of water, and incomplete sterilisation: twenty minutes' pasteurisation at 60° kills it. It is indifferently aerobic and anaerobic. Minimum temperature, 10°, optimum, 30°, maximum temperature, 45—46°. It develops readily in media containing sugars and nitrates.

It differs slightly in its biological reactions from the ordinary lactic ferments and although non-pathogenic for man and, apparently, animals, may be pathogenic for certain plants, for example, beetroots. G. W. R.

Nutritional Requirements of Yeast. III. Synthesis of Water-soluble-B. V. E. NELSON, ELLIS I. FULMER, and RUTH CESSNA (*J. Biol. Chem.*, 1921, **46**, 77—81).—A yeast was subcultured on alternate days throughout a year by adding 1 c.c. to 50 c.c. of a solution containing only salts and sucrose. The maximum concentration of original constituents was thus 1×50^{-180}. Yet it contained enough vitamin-B to restore rats fed on a synthetic diet to normal growth. It was therefore synthesised by the yeast. This further tends to invalidate Williams's method for estimating vitamin-B (compare *Ann. Rep.*, 1920, 167—168). G. B.

The Adaptation of a Top Yeast to a Galactose Fermentation Medium. H. VON EULER, I. LAURIN, and A. PETTERSSON (*Biochem. Zeitsch.*, 1921, **114**, 277—291).—Under normal conditions, the quotient of the velocities of fermentation of sucrose and of galactose by a top yeast (SBII) is 1 : 50. After a preliminary treatment of the yeast in galactose solutions the organism, however, becomes adapted to the galactose medium and the quotient of the velocities of fermentation of sucrose to that of galactose becomes 1 : 6·5. With a bottom yeast, the quotient of 1 : 2·4 was attained. As in the case of dextrose and lævulose, the addition of an aqueous extract of dried yeast accelerates the rate of the alcoholic fermentation of galactose. S. S. Z.

Constituents of *Pelvetia Wrightii*. KINSUKE KONDÔ (*J. Soc. Agric. Forestry, Sapporo*, 1920, **12**, 353—366).—From the product of hydrolysis of *Pelvetia Wrightii*, with 4% sulphuric acid, fucose and arabinose were isolated; the fucose gave 28·6% of methylfurfuraldehyde. The presence of pentosan (6·40%) and methylpentosan (2·04%) in the air-dried sample has been proved, but mannitol and galactan were not present. K. K.

Quantity of Hydrocyanic Acid in the Beans of *Phaseolus lunatus*. LÜHRIG (*Pharm. Zentr.-h.*, 1921, **62**, 95—97. Compare A., 1920, ii, 359, 411).—The quantity of hydrocyanic acid in these beans varies considerably; samples taken from separate sacks constituting a truck load yielded from 3·3 to 37·7 mg. of hydrocyanic acid per 100 grams of beans, the average being 20·1 mg. A composite sample from the whole of the 200 bags yielded 26 mg. per 100 grams. Sour milk did not liberate a further quantity of hydrocyanic acid after the beans had been distilled in the usual way to remove the acid. The author is of the opinion that there is no danger to health in consuming beans containing relatively large amounts of hydrocyanic acid, provided that they have been steeped in water for twenty-four hours, and that the water in which they are cooked is rejected; these treatments reduced the quantity of hydrocyanic acid to less than 1 mg. per 100 grams of beans. W. P. S.

Lobinol—A Dermatitant from *Rhus diversiloba* (Poison Oak). JAMES B. MCNAIR (*J. Amer. Chem. Soc.*, 1921, **43**, 159—164).—A poisonous substance has been isolated in the form of an amber-red, oily liquid from the bark of *Rhus diversiloba*, to which the author provisionally gives the name *lobinol*. If pure, it is apparently an unsaturated phenol, having two hydroxyl groups in the ortho position. It gives *acetyl* and *benzoyl* derivatives and a *benzyl ether*, an *α-naphthylurethane*, *phenylcarbamate*, and a *picrate*. It undergoes nitration, the product varying with the conditions. [See, further, *J. Soc. Chem. Ind.*, 1921, 276A]. W. G.

The Forms of Nitrogen in Soja Bean Nodules. W. H. STROWD (*Soil Sci.*, 1921, **11**, 123—130).—No trace of cyanogen ion could be found in soja bean nodules at the flowering or fruiting stage of the plant's growth. Of the total nitrogen in the nodules 30—40% was soluble in water and from 40—55% insoluble in 10% sodium chloride solution, or in 0·3% aqueous sodium hydroxide. The soluble proteins of the nodules contain apparently no globulin and only a small amount of albumin. About 3% of the water-soluble nitrogen was in the form of protein and proteose. Of the protein-free soluble nitrogen in the nodules about 16% of the total water-soluble nitrogen was present as amino-nitrogen and 19·3% was amide-nitrogen. More than 60% of the total water-soluble nitrogen was precipitated by phosphotungstic acid. The amount of the latter form, based on the percentage of total soluble nitrogen was much larger in the nodules than in roots, tops, or leaves. W. G.

Chemical Effect of Salts on Soils. W. P. KELLEY and A. B. CUMMINS (*Soil Sci.*, 1921, **172**, 139—159).—Chemically equivalent solutions of the chloride, sulphate, and nitrate of a given base produced substantially equivalent chemical reactions with the two soils studied. The solubility of the anion of the neutral salt solutions was not materially affected, but an exchange of bases took place. The different salts may be arranged in an ascending order of reaction: calcium, sodium, ammonium, potassium, magnesium. Calcium was the base most readily replaced from these soils. When solutions of phosphates were used considerable amounts of the phosphate ion was precipitated by each of these soils.

Chemical reactions take place between soils and alkaline solutions, which result in the conversion of a normal carbonate into a hydrogen carbonate, a lowering of the hydroxyl-ion concentration of the solution, and the precipitation of greater amounts of the kation of the solution than takes place with neutral solutions. The reactions between neutral salts and soils are dependent on the concentration.

The above facts need to be remembered in drawing conclusions from soil cultures as to the relative toxicity of different salts and the alkali tolerance of different plants. W. G.

Concentration of Potassium in Orthoclase Solutions not a Measure of its Availability to Wheat Seedlings. J. F. BREAZEALE and LYMAN J. BRIGGS (*J. Agric. Res.*, 1921, **20**, 615—621).—Finely-ground orthoclase containing 12·5% of potassium was shaken with distilled water, and germinated wheat seeds were floated on the surface of the mixture. The liquid contained 2—9 parts per million of soluble potassium. The amount of potassium in 100 seedlings after two to three weeks' growth was determined and compared with controls in solutions without potassium. The results showed that the seedlings absorbed no potassium from the solutions, although from potassium chloride solutions of the same concentration absorption took place readily. Addition of lime, gypsum, and carbon dioxide to the solutions did not render the potassium available, neither did boiling the solution. On the other hand, if the solution was filtered and oxidised by evaporation with acids, large amounts of potassium were absorbed by the plant. Further, if the solutions were filtered through a Pasteur-Chamberland filter to remove colloids and then oxidised, similar absorption took place. The experiments show that the potassium in orthoclase is combined in a complex form which is soluble in water but not available for plant use. The inference is drawn that the concentration of a plant food in a soil solution is not necessarily the measure of its availability to the plant. J. H. J.

Organic Chemistry.

Numerical Revision of the Results connected with the Density of Methyl Fluoride; Atomic Weight of Fluorine. E. MOLES and T. BATUECAS (*J. Chim. Phys.*, 1920, **18**, 353—358).—The authors have revised the calculations of their previously published work on the density of methyl fluoride and the atomic weight of fluorine (A., 1920, i, 283) and in the new calculations have used a more accurate value of *g*. From the revision the weight of the normal litre of methyl fluoride is shown to be 1·54507 grams; the weight calculated from determinations at 506·67 and 253·33 mm. respectively is 1·53576 and 1·52665 grams. This shows that the divergence from Avogadro's law, $1+\lambda=1{\cdot}01802$. The deviation of the compressibility between 0 and 1 atm. is 0·01771. The weight of the normal litre of oxygen determined under the same conditions as that of methyl fluoride is 1·42882 grams. From these data the molecular weight of methyl fluoride is calculated to be 34·025 and the atomic weight of fluorine $19{\cdot}002\pm0{\cdot}004$.
J. F. S.

The Catalytic Dehydrogenation of Alcohols. ERIC KEIGHTLEY RIDEAL (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 153—162).—In confirmation of Sabatier's experiments, the application of Nernst's theorem shows that the effect of temperature on the dissociation constants of the equilibria: $CH_3{\cdot}CHO+H_2 \rightleftharpoons C_2H_5{\cdot}OH$, and $CH_3{\cdot}CO{\cdot}CH_3+H_2 \rightleftharpoons CH_3{\cdot}CH(OH){\cdot}CH_3$, is very large. The velocity of decomposition at the surface of the solid catalyst is very much higher than the reverse reaction of hydrogenation. The variation of the dissociation constants with temperature was determined with a constant volume thermometer with reduced copper as catalytic material. Concordant values could not be obtained at atmospheric pressures, but a closer approximation to reversibility was obtained at low pressures. The value of ΔU_0 in Nernst's equation, for the decomposition of ethyl alcohol, was found to be 11,500 cal., the mean value deduced from the heats of combustion being 10,700 cal. In the case of *iso*propyl alcohol, the respective values are 21,300 and 11,800. In the latter case, an error of less than 1% in the heat of combustion would explain the discrepancy.
J. R. P.

The Catalytic Preparation of Mercaptans. R. L. KRAMER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 880—890).—The catalyst was prepared by immersing coarsely powdered pumice in a concentrated aqueous solution of thorium nitrate, using three parts of pumice to one part of thorium oxide, and evaporating the solution to dryness. The residue was dried at 120° and then heated in a current of air at 270° until decomposition was nearly complete, after which the temperature was raised to 400° to

complete the decomposition. Other processes did not yield an active catalyst.

Alcohol vapour and hydrogen sulphide, when passed in equimolecular proportions, at the rate of one gram molecule per hour over this catalyst at 380°, gave the following percentage yields of mercaptans: methyl, 41%; ethyl, 35%; propyl, 45%; butyl, 52%; *iso*butyl, 45%, and *iso*amyl, 47%. When attempts were made to purify the products by fractional distillation, it was found that propyl, butyl, and *iso*amyl mercaptans gave mixtures of constant boiling point with the corresponding alcohols, and ternary mixtures with the alcohols and water. These mercaptans were best purified through their lead salts. W. G.

The Interaction of Ethylene and Sulphur Monochloride. FREDERICK GEORGE MANN, WILLIAM JACKSON POPE, and RICHARD HENRY VERNON (T., 1921, **119**, 634—646).

The Intersolubility of ββ′-Dichlorodiethyl Sulphide and Ethyl Alcohol. THOS. G. THOMPSON, J. H. BLACK, and G. T. SOHL (*J. Amer. Chem. Soc.*, 1921, **43**, 877—879).—The critical temperature of solubility of ββ′-dichlorodiethyl sulphide and of absolute alcohol is 15·6°, but with 92·5% ethyl alcohol the value is 38·6°. Crude mustard gas may be purified by extraction with alcohol, and if the extract, after removal from the sulphur and resinous material, is cooled sufficiently, an excellent product is obtained. W. G.

Organic Derivatives of Tellurium. IV. Action of Ammonia and the Alkalis on α-Dimethyltelluronium Di-iodide. RICHARD HENRY VERNON (T., 1921, **119**, 687—697).

C_{18} Fatty Acids. I. The Non-identity of Elæostearic Acid Tetrabromide from Tung Oil with Ordinary Linolic Acid Tetrabromide. BEN. H. NICOLET (*J. Amer. Chem. Soc.*, 1921, **43**, 938—940).—α-Elæostearic acid tetrabromide is shown, contrary to the results of Kametaka (T., 1903, **83**, 1042), not to be identical with linolic acid tetrabromide. The mixed m. p., 103°, is lower than the m. p., 115°, of the two tetrabromides. *Ethyl tetrabromo-α-elæostearate,* m. p. 50°, is not identical with ethyl tetrabromolinolate. When brominated in light petroleum solution, α-elæostearic acid gave a *dibromide,* m. p. 85°, whereas linolic acid under similar conditions gave a tetrabromide only.

β-Elæostearic acid tetrabromide (compare Morrell, T., 1912, **101**, 2082) is identical with α-elæostearic acid tetrabromide. W. G.

Some Physico-chemical Constants of Acrylic Acid. CHARLES MOUREU and AUGUSTIN BOUTARIC (*J. Chim. Phys.*, 1920, **18**, 348—352).—The authors have determined the melting point, boiling point, density, heat of neutralisation, and heat of combustion of acrylic acid, and the electrical conductivity of solutions of acrylic acid and its sodium salt. The following data are recorded: melting point, 12·3°; boiling point, 141·6°/752 mm. and 48·5°/at 15 mm.

$D_{4^\circ}^{12^\circ}$, 1·0600, $D_{4^\circ}^{20^\circ}$, 1·0511; and the refractive index $n_D^{20^\circ}=1{\cdot}4224$. The heat of neutralisation is found to be 13·85 Cal., which shows that acrylic acid is a much stronger acid than formic and acetic acids. The heat of combustion is 4554·5 cal. per gram or 327·9 Cal. per gram-molecule, from which the heat of formation is calculated to be 93 Cal. The equivalent conductivity of sodium acrylate has been measured from dilution 32·4 to 1024 and the values found $v=32{\cdot}4$, $\Lambda=66{\cdot}5$; $v=64$, $\Lambda=68{\cdot}7$; $v=128$, $\Lambda=71{\cdot}3$; $v=256$, $\Lambda=73$; $v=512$, $\Lambda=74{\cdot}0$; and $v=1024$, $\Lambda=75{\cdot}2$; from these values Λ_∞ is extrapolated to the value 78·4. The ionic conductivity of the acryl ion is therefore 34·9. The equivalent conductivity of acrylic acid has been measured over the same range, and the degree of ionisation and the dissociation constant calculated at 18° $\Lambda_\infty=349{\cdot}9$, and $d=5{\cdot}6\times10^{-5}$. J. F. S.

Keto-enolic Desmotropy. XIV. Preparation of the Enolic Forms of Ethyl Acetoacetate and Acetylacetone. KURT H. MEYER and HEINRICH HOPFF (*Ber.*, 1921, **54**, [*B*], 579—580).—It has been shown by Meyer and Schoeller (A., 1920, i, 707) that highly enolised ethyl acetoacetate can be prepared by the fractional distillation of the ester from glass vessels without the exclusion of catalysts, whereas aseptic distillation from silica flasks leads to a separation of the two forms, which, under these conditions, do not undergo interconversion. The preparation of the pure ketone is readily effected in a single operation by the latter procedure. The isolation of the pure enol is now described. For this purpose, the equilibrium ester is distilled from a Jena glass vessel in the presence of a trace of phthalic acid. The distillate, which is collected in a quartz receiver, contains 88% of enol, and is immediately refractionated from a silica apparatus. The first fraction consists of pure enol and has n_D^{10} 1·4475, whereas Knorr (A., 1911, i, 516) gives n_D^{10} 1·4480. The enolic form of acetylacetone can be obtained in a similar manner; the final product contains about 1% of the ketone. The value calculated for n_D^{10} for the pure enol is 1·4625, whilst that derived from Knorr and Fischer's data (A., 1911, i, 976) is 1·4630. Aseptic distillation of the ketone gives a more highly enolised distillate and a more strongly ketonic residue, in which, however, the equilibrium condition is attained with extraordinary rapidity. Acetylacetone appears to be far more sensitive than ethyl acetoacetate to the influence of catalysts. H. W.

Ethyl Hydrogen Diethylmalonate. PHILIPPE DUMESNIL (*Compt. rend.*, 1921, **172**, 1043—1046).—Ethyl diethylmalonate is practically not attacked by alkalis in concentrated aqueous solution. In alcoholic solution, it is slowly hydrolysed, the process occurring in two stages. In the first, ethyl hydrogen diethylmalonate is produced and in the second diethylmalonic acid. These two reactions are bimolecular and at 85° the ratio of their velocities is $k/k'=11$.

Ethyl hydrogen diethylmalonate, m. p. 19°, may be isolated in the

pure state by distilling under a pressure of 1 mm. At the ordinary pressure, it begins to decompose at 14·0°, giving carbon dioxide and ethyl α-ethylbutyrate, $CHEt_2\cdot CO_2Et$. W. G.

A Method for the Degradation of Acids of the Glutaric Series. A. Windaus and F. Klänhardt (*Ber.*, 1921, **54**, [*B*], 581—587).—Considerable difficulties are experienced in elucidating the constitution of hydroaromatic acids of the glutaric series, since they are exceptionally resistant to oxidising agents and do not suffer smooth thermal degradation. It is now shown that they exhibit a characteristic behaviour when their silver salts are treated with iodine, since they are converted into mixtures of the corresponding anhydride and the lactone containing one fewer atom of carbon, thus: $O\cdot CO\cdot[CH_2]_3\cdot CO\cdot O = \underbrace{CO\cdot[CH_2]_3\cdot CO}_{O} + O$ and $O\cdot CO\cdot[CH_2]_3\cdot CO\cdot O = \underbrace{CO\cdot[CH_2]_2\cdot CH_2}_{O} + CO_2$. The yield of pure lactone varies somewhat with the individual member and the temperature of the reaction, but may reach 40%. The following method of elucidating the position of the carboxyl group in aliphatic dicarboxylic acids is advocated. The acid is evaporated with acetic anhydride and the residue heated at 260—280°; the smooth formation of a ketone shows the presence of a pimelic or adipic acid, whilst the ready production of an anhydride which is stable at this temperature indicates a glutaric or succinic acid. The silver salt is then heated with iodine when the presence of the former is shown by the production of a lactone, whereas the latter gives only the anhydride.

Equivalent amounts of the finely-divided silver salt and iodine are mixed with sand and heated slowly at about 150°; the cold product is extracted with ether, and the ethereal solution is agitated with cold concentrated potassium carbonate solution containing a little sodium sulphite which dissolves the anhydride in the form of the glutarate without affecting the lactone.

Glutaric acid gives γ-butyrolactone, b. p. 202—203° in 30% yield. ββ-*Dimethyl-γ-butyrolactone*, b. p. 207—208°, m. p. 55—57° is obtained from ββ-dimethylglutaric acid and is oxidised by potassium dichromate to αα-dimethylsuccinic acid, m. p. 140°. α-Ethylglutaric acid is transformed into *γ-hexolactone*, b. p. 215—216°, the constitution of which is deduced from its conversion into barium γ-hydroxyhexoate and its oxidation to succinic acid; the product does not appear to contain α-ethyl-γ-butyrolactone. αα′-Diethylglutaric acid is converted into *α-ethyl-γ-hexolactone*, b. p. 231—233°, which is characterised by its oxidation to α-ethylsuccinic acid.

H. W.

Preparation of Galactonolactone. P. A. Levene and G. M. Meyer (*J. Biol. Chem.*, 1921, **46**, 307—308).—The pure unimolecular lactone is prepared by suspending calcium galactonate in water containing an equivalent of oxalic acid, filtering, concentrating under reduced pressure until a crystalline deposit begins to

form, redissolving this by warming, and pouring the syrupy liquid into glacial acetic acid. The hydrated form of the lactone, with $1H_2O$, crystallises. G. B.

The Humus Acids. SVEN ODÉN (*Koll. Chem. Beihefte*, 1919, **11**, 75—260).—A long account of the humus acids which contains a very full account of all previous work, a bibliography of the subject containing 386 references, and an account of some new work of the author. Humus substances are defined as those yellowish-brown to dark brownish-black substances of unknown constitution which are produced by the decomposition of organic substances either in nature or artificially. They show a marked affinity for water, and when insoluble in water are at least dispersed or undergo swelling. The water which is taken up is lost when the substances are brought under a diminished pressure. Humic acids are those humus substances which are capable of separating a hydrogen ion and which, with strong bases, produce typical salts with the separation of water. Humus acids consist of three members, (*a*) humic acid, (*b*) hymatomelanic acid, and (*c*) fulvic acid, and the general properties of the three acids are tabulated. The second chapter deals with the history of the study of these substances and with the work published between 1826 and the present day. The preparation of humic acid from peat is described and the methods of purification are dealt with. It is shown that when ammonia acts on aqueous suspensions of leaf-mould and on humified leaf mould an adsorption compound with the ammonia can be recognised. At the same time, the dark brown substance enters largely into a salt formation and even at concentrations as low as $0{\cdot}01N$ the salt formation predominates largely over the adsorption. With increase of temperature, the velocity of the humate formation increases. Electrometric titrations lead to the approximate value 340 ± 10 for the equivalent weight of the humic acid. This value is confirmed by conductivity titrations and by the analysis of the calcium and barium salts. The equivalent conductivity of sodium humate solutions is found to be: at 15°, $\Lambda_\infty = 83$, and at 17°, $\Lambda_\infty = 90$. By measurement of the electrical conductivity it is shown that the dried and insoluble humic acid is very slowly converted into the soluble ammonium humate, the process being far from complete in forty-six days. Viscosity measurements of solutions of humic acid in sodium, potassium, lithium, and ammonium hydroxide, taken together with the equivalent conductivity (Ostwald's rule), indicate that humic acid is tetrabasic. The greater the degree of dispersion of humic acid suspensions, the greater the absorption of light, that is, the greater the intensity of the colour, but with the formation of the humate ion the intensity of the colour becomes much greater. In the case of sodium humate, the absorption maximum lies at 250 $\mu\mu$. Humic acid has a medium strength, is generally sparingly soluble in water, and readily forms colloidal solutions; it has a composition which is to be represented by $C_{60}H_{52}O_{24}(CO_2H)_4$. A number of metallic salts of humic acid are described. Chapter IV

of the work deals with the hymatomelanic acid and the process of humification. Hymatomelanic acid has a yellowish-brown colour, and it absorbs light less than humic acid. It has an equivalent weight of about 200; the salts of this acid are all insoluble in alcohol, but they easily form highly dispersed suspensions. Humus colloids are shown to exercise a considerable protecting action on clays which is of the same order as that of other protecting colloids, but is specific to certain varieties of clay and electrolytes. The hydrogen-ion concentration of aqueous extracts of turf is found to vary between $0{\cdot}8\times10^{-4}$ and $6{\cdot}6\times10^{-4}N$. The significance of "liming" the humoid earth is considered. It is shown that limed samples always bind more water than unlimed samples, but the difference is not of practical importance; the limed humus, however, gives up its water more readily than the unlimed humus. After liming, the water appears to be a little more firmly held and consequently is less easily taken up by plants. J. F. S.

Distillation of Aqueous Solutions of Formaldehyde. JOHN A. WILKINSON and I. A. GIBSON (*J. Amer. Chem. Soc.*, 1921, **43**, 695—700).—Aqueous solutions of formaldehyde of various compositions have been distilled and the various fractions analysed. From the data thus obtained distillation curves have been plotted. It is shown that with small concentrations of formaldehyde (below 8%) the distillate always contains a greater percentage of formaldehyde than the original solution, but with higher concentrations the distillate is always weaker than the original solution. With low concentrations, the residue in the distilling flask is always weaker than the distillate which has just passed over, but with higher concentrations the residue is always stronger. The difference is accounted for by the polymerisation of the formaldehyde in water solutions into molecules having a low vapour pressure. Prolonged heating does not form any more of the solid polymeride than is formed normally, since the distillation curves of a given solution which had been boiled for twenty-four hours with a reflux condenser and the solution which had not been previously boiled, were identical. J. F. S.

The Action of Unimolecular Formaldehyde on Grignard's Compounds. K. ZIEGLER (*Ber.*, 1921, **54**, [*B*], 737—740).—The production of primary alcohols by the action of Grignard's reagents on trioxymethylene is rendered tedious by the sparing solubility of the latter in ether and its very gradual depolymerisation. The difficulty is avoided by conducting the vapours from thoroughly-dried, boiling trioxymethylene into the cold, well-stirred Grignard compound. The yields are generally better than those obtained in the older process and attain their maxima in the cases of benzyl alcohol and α-naphthylcarbinol, b. p. 162—163°/11 mm., m. p. 59·5—60°. The production of *n*-propyl alcohol from magnesium ethyl bromide is rather less satisfactory, partly, at any rate, owing to the formation of considerable quantities of diethyl methylene ether, $CH_2(OEt)_2$. H. W.

Preparation of Acetaldehyde from Acetylene. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (Brit. Pat. 143891).—In the conversion of acetylene into acetaldehyde in presence of mercury compounds, the catalyst is continuously regenerated in the absorption vessel itself by an anodic oxidation process in which the reduced mercury forms the anode, the acid reaction liquid the electrolyte, and mercury, lead, or platinum the cathode. The latter may either be arranged in a chamber closed by a diaphragm from which the hydrogen is discharged, or it may be placed without a diaphragm in the acid reaction liquid, the hydrogen which gradually accumulates in the circulating gas being removed at intervals. By this process larger quantities of mercury salt exceeding 10% of the weight of the reaction liquid can be employed with a consequent increase in the rate of absorption of the acetylene. G. F. M.

Acraldehyde. CHARLES MOUREU, CHARLES DUFRAISSE, ADOLPHE LEPAPE, PAUL ROBIN, JEAN POUGNET, AUGUSTIN BOUTARIC, and ETIENNE BOISMENU (*Ann. Chim.*, 1921, [ix], **15**, 158—211).—A more detailed account of work already published (A., 1919, i, 574; 1920, i, 10, 143, 144). W. G.

Some Physico-chemical Constants of Acraldehyde. CHARLES MOUREU, AUGUSTIN BOUTARIC, and CHARLES DUFRAISSE (*J. Chim. Phys.*, 1920, **18**, 333—347).—The authors have determined the melting point, boiling point, vapour pressure, density, coefficient of expansion, refractive index, molecular refraction, solubility in water, specific heat, latent heat of vaporisation, heat of combustion, and electrical conductivity of acraldehyde. The material used was very pure and the data given, with the exception of the electrical quantities, are in the highest degree trustworthy. The melting point lies between −88° and −87°, the boiling point is 52·15°/751·3 mm., 52·46°/760 mm., and 53·00°/773·2 mm. The vapour pressure has been determined over the range 3·3—137·2° and the results are given in kilogr./sq. cm.; the following values are recorded: 3·3°, 0·135; 5°, 0·148; 10°, 0·187; 15°, 0·235; 25°, 0·366; 40°, 0·645; 50°, 0·923; 60°, 1·17; 70°, 1·56; 80°, 2·14; 90°, 3·045; 100°, 4·18; 110°, 5·35; 120°, 6·91; 130°, 8·69; and 137·2°, 10·0. The density has been measured at temperatures from 0° to 50°, and is given by the formula $D_t=0{\cdot}86205/(1+0{\cdot}001318t+0{\cdot}0000033t^2)$; actual measured values are 0°, 0·86205; 15°, 0·8447; 30°, 0·8269; and 50°, 0·8075. The molecular volume at the boiling point is 70·0 and the mean coefficient of expansion over the range 0—49° is given by the formula $\delta=0{\cdot}001318+0{\cdot}0000033t$. The following values of the index of refraction are given: n_D; 11·5°, 1·4066; 15°, 1·40475; 16·2°, 1·4041; 19·3°, 1·4022, and the molecular refractivity is 16·24. The solubility of acraldehyde in water and water in acraldehyde has been determined over the range −8° to +53°. The results show that water becomes more soluble in acraldehyde as the temperature is raised, whilst acraldehyde becomes less soluble. The mean specific heat over the range 17—40° is 0·5115; 17—47°, 0·5105; and 18—44°, 0·5115. The latent heat of vaporisation at the boiling point is

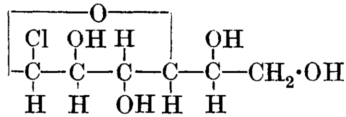
120·7 cal. per gram, the molecular latent heat 6759·2 cal. This gives the value 20·76 for the constant ML/T. The molecular heat of combustion at constant volume is 389·8 Cal. at constant pressure, 390·1 Cal. and the heat of formation is given by $3C_{(diamond)}+4H+O=C_3H_4O_{liquid}+30·8$ Cal. The electrical conductivity is given as $1·55\times10^{-7}$ reciprocal ohms at 10°. Acraldehyde is not a good ionising medium, for a solution of 0·088 gram of benzoic acid in 100 c.c. of acraldehyde has a conductivity of only 2×10^{-7} reciprocal ohms. J. F. S.

Preparation of Glyoxal by the Action of Acetylene on Gold Chloride or Bromide. KARL KINDLER (*Ber.*, 1921, **54**, [*B*], 647—649).—Gold is quantitatively precipitated from aqueous solutions of auric haloids by acetylene if the gold content does not greatly exceed 1·5%. The acetylene is thereby converted into carbon dioxide (12%) and glyoxal (about 86%), the latter appearing to be the sole organic product of the change. The finely-divided gold can be readily reconverted into the haloid by treatment with chlorine or bromine. H. W.

Researches on Residual Affinity and Co-ordination. III. Reactions of Selenium and Tellurium Acetylacetones. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1921, **119**, 610—625).

Compounds of Dextrose with Salts. W. D. HELDERMANN (*Arch. Suikerind. Ned. Ind.* [*Chem. Serie*], 1920, 2305—2310; from *Chem. Zentr.*, 1921, i, 783).—Double salts of dextrose with potassium chloride, sodium chloride, and potassium sulphate do not occur in aqueous solution at 30°; the transformation point for such double salts may, however, lie below 30°. G. W. R.

α-Glucosyl Chloride and a New Disaccharide (α-Glucosidoglucose). AMÉ PICTET and PIERRE CASTAN (*Helv. Chim. Acta*, 1921, **4**, 319—324).—Glucosan dissolves in concentrated hydrochloric acid with development of heat and formation of a compound, $C_6H_{11}O_5Cl$, which is obtained as a colourless, transparent, vitreous mass and is named *α-glucosyl chloride*. When heated with acetic anhydride and sodium acetate this compound is converted into α-acetochloroglucose, whilst sodium methoxide in alcoholic solution converts it into α-methylglucoside. The chlorine atom is, therefore, attached to the first carbon atom of the glucose chain, its spacial position being in correspondence with glucosides of the α-series. If the structure previously proposed for glucosan (A., 1920, i, 820) is adopted, α-glucosyl chloride will have the annexed configuration.



The chloride dissolves, readily and without change, in cold water, the solution giving a precipitate with silver nitrate only in the hot.

The mobility of the chlorine atom renders possible the utilisation of α-glucosyl chloride for the synthesis of other glucosides and disaccharides of the α-series. Treatment of

glucosan in methyl alcoholic solution with alcoholic potassium hydroxide yields a *potassium* derivative of glucosan, $C_6H_9O_5K$, which is highly hygroscopic, but, if filtered rapidly and washed with dry ether, may be kept for a long time out of contact with moisture. The interaction of this potassium derivative and α-glucosyl chloride yields a *glucosylglucosan* (not isolated) which by union with water forms *α-glucosidoglucose*, $C_{12}H_{22}O_{11}$ (annexed formula ?); this exhibits the normal cryoscopic behaviour in aqueous solution, separates in crystalline crusts, has m. p. 90°, and on further heating swells and loses water, resolidifies, and melts again at 187°. It has a bitter taste and exhibits mutarotation, the value of $[\alpha]_D$ being initially $+12{\cdot}02°$ and finally $+10{\cdot}51$ to $10{\cdot}54°$.

$$\begin{array}{l} \overbrace{\quad\quad\quad\quad\quad\quad}^{O} \\ OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH{\cdot}[CH_2{\cdot}OH]_2{\cdot}CH \\ OH{\cdot}CH{\cdot}[CH(OH)]_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2 \\ \underbrace{\quad\quad\quad\quad\quad\quad}_{O} \end{array}\!\!>O$$

It fails to redden decolorised magenta solution and reduces Fehling's solution in the hot, its reducing power being 59·9% of that of dextrose; it is converted completely into the latter sugar when boiled with hydrochloric acid. α-Glucosidoglucose is not hydrolysed by emulsin, forms a *phenylosazone*, m. p. 173—174°, and in some respects resembles, but is not identical with, gentiobiose.

T. H. P.

Polysaccharides. VII. Constitution of Cellobiose. P. Karrer and Fr. Widmer (*Helv. Chim. Acta*, 1921, **4**, 295—297).—Hydrolysis of heptamethyl-β-methylcelloside (this vol., i, 310) by means of 5% hydrochloric acid solution yields tetramethyl- and trimethyl-glucoses (compare Denham and Woodhouse, T., 1914, 2357; 1917, 244; Haworth and Leitch, T., 1918, 188). Since heptamethyl-β-methylcelloside is obtained by methylation of cellobiose, the latter must, in accordance with the formulæ for tri- and tetra-methylglucoses, be 5-β-*d*-glucosido-*d*-glucose,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}\overbrace{CH{\cdot}[CH(OH)]_2{\cdot}CH}^{O}{\cdot}O{\cdot}CH(CH_2{\cdot}OH){\cdot}\overbrace{CH{\cdot}[CH(OH)]_2{\cdot}CH}^{O}{\cdot}OH.$$

In a paper published since the completion of the authors' work, Haworth and Hirst (T., 1921, **119**, 193) have also given this structure for cellobiose, but the heptamethyl-β-methylcelloside they used contained admixed heptamethyl-α-methylcelloside. T. H. P.

The Fundamental Organic Substance of Amylopectin. M. Samec and Anka Mayer (*Compt. rend.*, 1921, **172**, 1079—1082).—The classification suggested for the products of hydrolysis of starch is:—amyloses (without reducing power), dextrins (with reducing power), dextrinic acids (with acid action), prefixing these names by amylo-, erythro-, or achroo-, according as they give blue, red, or no colour with iodine. In this manner the carbohydrate derived from amylopectin will be classed as an erythroamylose. W. G.

Plant Colloids. VIII. Some Cellulose Dextrins. M. Samec and J. Matula (*Koll. Chem. Beihefte*, 1919, **11**, 37—73. Compare A., 1919, i, 472).—The degradation of cellulose sulphite by sulphuric acid (85—50%) and phosphoric acid (85—76·5%)

has been investigated. In the case of the first named acid, the action was carried out at 20°, whilst in the latter case temperatures of 50° and 70° were employed. The reactions were allowed to proceed for periods up to one hundred and forty-four hours, and the product was examined at intervals by means of determinations of the colour produced by iodine, the viscosity, the amount precipitated by alcohol or water, the optical rotation, and the solubility in sodium hydroxide (10%). The results of the experiments with sulphuric acid are presented in numerous tables, and show that 50% sulphuric acid does not completely dissolve cellulose sulphite, whilst acid of concentrations greater than 85% chars it. The freshly-prepared cellulose solutions in sulphuric acid are at first colourless, but they become coloured when kept. The iodine coloration changes from pure blue to violet and then to reddish-brown, and finally disappears as the extent of the degradation becomes greater. The relative viscosity rises to a maximum and then falls as the swelling and solution processes increase; the rate of the change in the viscosity increases with increasing acid concentration. The fall in the viscosity after the maximum has been reached points to a degradation of the molecule. The extent to which the cellulose degradation products are precipitated by water and alcohol is an excellent means of following the extent of the degradation. A portion of the dextrin is soluble in water. All concentrations of sulphuric acid above 60% destroy the gelatins which are insoluble in water within the first half hour after the reaction has commenced. This destruction also takes place in the more dilute acids, but the more slowly the more dilute the acid. The products produced by 75—85% acid in half an hour are completely soluble in alcohol. On heating the alcoholic solution, the esters primarily formed are decomposed and a thick, white precipitate separates. The degradation products formed by 65—55% acid give a transparent very stiff jelly with alcohol, which on boiling with alcohol diminishes in viscosity and deposits dextrin as a white, flocculent mass. The progress of the degradation of cellulose is shown by (1) the changes in the iodine reaction, (*a*) change of the blue colour to violet, (*b*) change of the violet colour to brown, and (*c*) disappearance of the colour, (2) the change of products in a water-soluble condition, and (3) the precipitation by alcohol, (*a*) the dextrin esters gelatinise with alcohol and the dextrin is then precipitated, (*b*) the dextrin esters and the dextrins are insoluble in alcohol, (*c*) the dextrin esters are soluble but the dextrins insoluble in alcohol, and (*d*) both the dextrin esters and the dextrins are soluble in alcohol.

The degradation by phosphoric acid proceeds differently from that with sulphuric acid. At ordinary temperatures phosphoric acid of a greater concentration than 75% forms a colourless, very viscous jelly which is only very slowly changed at this temperature. At higher temperatures, the decreasing viscosity and increasing coloration of the solution indicate a degradation, but the velocity of the change is very much less than in the case of sulphuric acid. Thus the blue iodine colour is still given by the products after the

reaction has been proceeding for many hours with 85% phosphoric acid at 50°, the first shade of violet appearing only after sixteen hours. A more rapid degradation takes place at 70°. The production of water-soluble products occurs in forty-six hours, whereas this is the case in one hour with 60% sulphuric acid at the ordinary temperature. The phosphoric acid-cellulose jellies are extremely viscous, which indicates, not only a small velocity of degradation, but also a very complete esterification of the dextrins. At 70°, the solution of the cellulose occurs rapidly, but the mixture speedily becomes dark brown or black. The author has isolated five dextrin products which have been examined as to their viscosity, precipitation by salts, hydrogen-ion concentration, conductivity, and osmotic pressure. These products are characterised "Dextrin I," a product soluble in sodium hydroxide, insoluble in water, prepared by the action of 50 parts of 55% sulphuric acid on 2 parts of cellulose at 20° for forty-five minutes; "Dextrin II," a product prepared similarly, but soluble in water and insoluble in alcohol; "Dextrin III," a product prepared from 2 parts of cellulose and 5 parts of 55% sulphuric acid, which is soluble in water and insoluble in alcohol; "Dextrin IV," prepared by the action of 1 part of cellulose and 20 parts of 85% phosphoric acid for one hour at 50°, and "Dextrin V," prepared by the action of 25 parts of 80% phosphoric acid on 1 part of cellulose for twenty-four hours at 50°. All five products were dialysed until free from electrolytes, a process which occupied many weeks. The examination of the various dextrins shows that the action of the sulphuric acid depends, not only on the concentration of the acid, but also on the relative quantities of cellulose and acid. With a sufficient excess of acid, dialysable dextrins are produced in the first quarter of an hour and at the same time the molecular weight of the colloidal residue is greatly diminished. By further action of the acid, the degradation both of the dialysable portion and of the colloidal residue continues until, after five hours, the most coarsely disperse portion has a mean molecular weight of 2400 and the viscosity falls from 1·5 to 1·1; at the same time, the group $-SO_4H$ enters the molecule with the formation of esters. On adding sodium hydroxide to the dextrin solution a portion of the hydroxide is bound, which in the case of "Dextrin I" is found to be one molecule of hydroxide to an amount of dextrin corresponding with about 41—42$C_6H_{10}O_5$ groups, and in the case of "Dextrin III" one molecule of hydroxide to about $6C_6H_{10}O_5$ groups. This increase in the amount of bound hydroxide is taken to indicate an increase in the number of HSO_4' groups in the molecule. Assuming that in the neutralisation, with phenolphthalein as indicator, only the $-SO_4H$ group is concerned, then one such group is combined with 41—42$C_6H_{10}O_5$ groups in "Dextrin I," whilst in "Dextrin III" the complex $C_{36}H_{59}O_{30}\cdot SO_4H$ is present.

The action of diastase on the five dextrins has been examined. "Dextrin I," in the form of a suspension, is not markedly attacked by diastase, but in colloidal solution its reducing powers are markedly reduced and a two hours' interaction reduces the copper number from 15·8 to 6·9, and at this point the dextrin flocculates. "Dextrin

II" is relatively more like the starches in its behaviour with diastase. The viscosity decreases strongly and the reducing power increases, and after two hours' action a fermentable sugar is produced. The optical rotation increases, whilst the electrical conductivity and the hydrogen-ion concentration remain constant. "Dextrin III" behaves similarly to "Dextrin II," but here the conductivity and the hydrogen-ion concentration increase. "Dextrin IV" is not attacked, whilst "Dextrin V" behaves similarly to the corresponding sulphuric acid product except that the amount of action is less.

J. F. S.

Plant Colloids. X. Action of Formaldehyde on Starch. M. Samec and Anka Mayer (*Koll. Chem. Beihefte*, 1920, **13**, 165—192. Compare preceding abstract).—The action of formaldehyde solutions of various concentrations on potato starch has been investigated at various temperatures. It is shown that formaldehyde does not effect a degradation of starch at the ordinary temperature, but converts it into a loose compound, which has lost its power of giving a coloration with iodine and is much more hydrated than starch itself. The mean molecular weight of formaldehyde-starch is the same as that of natural starch, and the content of starch of lower molecular weight compounds is not changed by the addition of formaldehyde. The density of formaldehyde-starch solutions is somewhat greater than that of ordinary starch solutions, but the decrease in volume is not great enough to mask the increase in the viscosity. Formaldehyde is not capable of bringing about a resynthesis from the degradation products of starch. At higher temperatures, a degradation takes place in formaldehyde-starch solutions to an extent which is governed by the amount of acid formed by oxidation. The optical rotation of natural starch is slightly decreased by the action of formaldehyde. The change in properties brought about by formaldehyde is practically the same as that produced by the action of a $5-10\times10^{-3}N$ potassium hydroxide solution, and both can be explained by an opening of the oxygen ring and a subsequent combination with the reacting agent. Formaldehyde reacts with amylopectin and with amylose in an analogous manner and does not affect the relationship of the quantities of these substances. J. F. S.

Cellulose. Karl Freudenberg (*Ber.*, 1921, **54**, [*B*], 767—772).—It is shown that cellobiose octa-acetate can be isolated in a yield corresponding with the presence of 35—36% of cellobiose in the original material in a single operation when cellulose is treated with a mixture of acetic anhydride and concentrated sulphuric acid at a low temperature, the operation then requiring about fourteen days. The yield is thus but little lower than the highest values recorded by Ost (A., 1906, i, 560) and Madsen (*Diss.*, Hanover, 1917). In order to gain an idea of the amount of octa-acetate actually produced, the author considers the process to be divisible into three stages: (1) from the commencement of the reaction until such time as the cellulose is so far dissolved and swollen that it is completely penetrated with sulphuric acid (about eight hours); (2) from

this point until the bulk of the octa-acetate has separated, and (3) the period until the conclusion of the experiment. Losses in the octa-acetate are occasioned in the second phase by the action of sulphuric acid on the dissolved substance, and in the third phase by the degradation of the crystallised material. An estimate of the extent of these losses is obtained by subjecting the octa-acetate dissolved in chloroform to the action of the acid mixture of such a concentration as corresponds to that of the final stage of acetolysis and by exposing the crystals to the action of the acid mixture. The results lead the author to the conclusion that cellulose is composed to an extent of more than 60% of cellobiose.

This result is in contradiction with Hess's hypothesis (A., 1920, i, 532, this vol., i, 12) that cellulose is fundamentally composed of pentaglucosidylglucose, in which case the maximal yield would be 32·7%. Although, however, cellobiose is to be regarded as the unit of cellulose, it is remarkable that the yield of isolable octa-acetate is considerably below 50% of that theoretically possible, and it appears very difficult to improve this value. This may be explained on the hypothesis that the molecule is composed of a series of cellobiose residues which are all united on the same principle as cellobiose itself. Calculations based on the law of probability indicate that the disruption of a uniform polysaccharide chain of ten or more members in homogeneous solution would only lead to the isolation of about 32% at most in the form of biose, whilst if the latter crystallised as it was formed and then remained completely intact the yield would be increased to 67%. H. W.

Cellulose. III. Asymmetric Structure of Cellulose and the Influence of Ammoniacal Copper Hydroxide [Schweizer's Reagent] on the Rotation of Carbohydrates. KURT HESS and ERNST MESSMER (*Ber.*, 1921, **54**, [*B*], 834—841).—The optical activity of cellulose was a subject of discussion about thirty-five years ago between the French chemists Levallois (A., 1885, 500), and Béchamp (A., 1885, 257, 500); the former observed that solutions of the carbohydrate in ammoniacal copper hydroxide were optically active and attributed this result to the cellulose. The latter found that freshly regenerated, and therefore unhydrolysed, cellulose was inactive and considered the activity of the copper solution to be due to the latter itself, since he observed activity with such solutions in the absence of cellulose although his values lie within the limits of his experimental error. A repetition of the experiments has confirmed Levallois's results; cellulose-free, ammoniacal copper hydroxide solutions are optically inactive. The experimental work is particularly difficult since for blue light even with long experience it is not easy to avoid an error of $\pm 0{\cdot}05°$ in setting the polarimeter and, also, the rotation dispersion is particularly large, although it can be partly compensated by suitable use of a subsidiary Schweizer's solution. Solutions of cellulose in the latter are optically active, two determinations under somewhat differing conditions giving the values $[\alpha]$=about $-950°$ and $-1000°$ respectively. On the other hand, solutions of "regenerated"

cellulose in concentrated hydrochloric acid are inactive, as are also ethereal solutions of ethylcellulose, aqueous-alkaline solutions of xanthogenate cellulose, and jellies of cellulose in neutral salt solutions. Cellulose presents, therefore, a marked example of "latent asymmetry," thus resembling mannitol, and it would thus appear that ammoniacal copper hydroxide behaves towards it in the same manner as boric acid or borax towards the simpler carbohydrates. The phenomena may possibly be explained by the hypothesis that the subsidiary valencies which unite the celluxose in cellulose are diverted by the copper atom with consequent disruption of the cellulose molecule and formation of an ammoniacal copper celluxose complex to which the activity of the solution is due. This hypothesis is supported to some extent by the observation that the specific rotation of sucrose in Schweizer's reagent at first diminishes with increasing copper content until it becomes zero, when 3 molecules of the carbohydrate are present for every 5 molecules of copper, and subsequently increases. A marked displacement of activity is similarly observed with α-methylglucoside. H. W.

Experiments on Wood Cellulose. WATSON G. HARDING (*J. Physical Chem.*, 1921, **25**, 201—203).—If wood cellulose is heated at about 100° with dilute sodium hydroxide for a sufficient time the rate of attack becomes very low and may become zero. With the sample of wrapping paper studied, heating with 1% sodium hydroxide for twenty-five hours left about 60% of material undecomposed. The sodium hydroxide did not decompose all the ligno-cellulose, and may not have decomposed any. Approximately equal decomposition may be obtained by heating for about six hours with 6% sodium hydroxide. J. R. P.

Nature of the Process of Swelling. I. E. KNOEVENAGEL and OTTO EBERSTADT (*Koll. Chem. Beihefte*, 1921, **13**, 194—212).—A large number of experiments on the swelling of acetylcellulose are described. It is shown that in pure water and in absolute alcohol acetylcellulose does not swell to a measurable extent, but when mixtures of alcohol and water or water and acetone or acetic acid are used it swells strongly. There is for each pair of liquids a definite composition at which the swelling is at a maximum. The amount of swelling was measured in the first place by the increase in the weight of the hair-like fibres after soaking in the liquid. The amount of swelling did not decrease when the whole of the organic solvent was displaced from the swollen mass by water, that is, when the swollen mass was converted into the pure hydrogel. The amount of swelling was also determined by the increase in volume, which was ascertained from microscopic measurements of the diameter of the individual fibres. Both methods gave similar results. Unswollen acetylcellulose is only slowly dyed in 0·05% aqueous solutions of methylene-blue at 25°; the maximum of coloration for dull tones was reached only in the course of several months, whilst strongly swollen acetylcellulose reached the same colour maximum under identical conditions in a very few minutes.

An increase in temperature accelerated the dyeing. Unswollen acetylcellulose is hydrolysed by aqueous solutions of alkali hydroxides with the greatest difficulty even at elevated temperatures, whilst swollen acetylcellulose is completely hydrolysed at 25° in half an hour by $N/2$ potassium hydroxide. As in the case of the dyeing, the velocity of hydrolysis increases with the degree of the swelling. The behaviour of dilute solutions of potassium hydroxide with swollen acetylcellulose enables the amount of the acetyl group present to be easily estimated. J. F. S.

The Production of Carbon Monoxide by the Action of Alkaline Hypohalogenites on Carbamide. WILLIAM HOLDSWORTH HURTLEY (*Biochem. J.*, 1921, **15**, 11—18).—The author arrives at results similar to those of Krogh (A., 1913, ii, 641) with regard to the production of carbon monoxide by the action of alkaline hypobromite or hypochlorite on carbamide. Under ordinary experimental conditions he finds 0·7% of carbon monoxide in the gas evolved from a 2% solution of carbamide. The question of the origin of the carbon monoxide is discussed in some detail, and experiments are described which show that carbon monoxide is contained in the gases evolved during the action of ammonia and sodium hydroxide on dichlorocarbamide; and when sodium hypobromite reacts with semicarbazide, hydrazodicarbonamide, azodicarbonamide, and acetylcarbamide. It is suggested that (in accordance with an observation of Fenton) some of the carbamide is converted into cyanate, which in turn gives rise to the above series of compounds and hence to the carbon monoxide. C. R. H.

Passage from Guanidine to Cyanamide and from Diguanide to Dicyanodiamide. GUIDO PELLIZZARI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 171—175).—By the addition of ammonia (1 mol.), cyanamide is converted into guanidine and dicyanodiamide into diguanide. The only known reaction occurring in the opposite sense is the transformation of *o*-phenylenediguanide into β-cyano-*o*-phenyleneguanidine by treatment with nitrous acid (this vol., i, 362). This treatment has now been extended to other compounds, and it is found that nitrous acid converts diguanide into cyanoguanidine or dicyanodiamide, $NH[C(NH)\cdot NH_2]_2+HNO_2=NH_2\cdot C(NH)\cdot NH\cdot CN+N_2+2H_2O$, and guanidine similarly yields a small proportion of cyanamide. Although the ammonia is liberated as nitrogen and water, which are the decomposition products of ammonium nitrite, there are indications that the nitrous acid does not directly detach a molecule of ammonia, but that an intermediate compound is formed. In the case of guanidine, this intermediate compound has been identified with nitrosoguanidine (compare Thiele, A., 1893, i, 389), the formation of which represents a reversible reaction, $NH:C(NH_2)_2+HNO_2 \rightleftharpoons NH:C(NH_2)\cdot NH\cdot NO+H_2O$; the mechanism of the reaction in the other two cases is probably similar. T. H. P.

The Preparation of Cyanogen Bromide and Iodide. V. GRIGNARD and P. CROUZIER (*Bull. Soc. chim.*, 1921, [iv], **29**, 214—217).—An aqueous solution of sodium cyanide is run slowly with constant stirring on to bromine or iodine covered with a small amount of water, the temperature not being allowed to rise above 25°, until the colour due to the bromine or iodine has disappeared. Chlorine is then passed into the liquid and at the same time more sodium cyanide is run in, the liberated bromine or iodine being in slight excess, until the end of the operation, when a very slight excess of the cyanide is added. For the recovery of cyanogen bromide, it may either be filtered off or the liquid may be distilled, the vapour being passed over anhydrous calcium chloride at 80°. In the preparation of cyanogen iodide, the latter is extracted with ether and the solvent distilled off. W. G.

Trimethylphosphine and its Selenide. R. R. RENSHAW and F. K. BELL (*J. Amer. Chem. Soc.*, 1921, **43**, 916—919).—The authors have prepared trimethylphosphine by the two methods described by Hofmann (*Annalen*, 1857, **104**, 29; *Ber.*, 1871, **4**, 209, 373). They find that the selenide obtained by shaking trimethylphosphine in ethereal solution with precipitated selenium has m. p. 140° (corr.) (Hofmann, *loc. cit.*, gives m. p. 84°). W. G.

Organic Compounds of Arsenic. II. Action of Cyanogen Bromide on Triethylarsine. WILHELM STEINKOPF and JOHANNES MÜLLER (*Ber.*, 1921, **54**, [*B*], 841—847. Compare Steinkopf and Mieg, A., 1920, i, 537).—Triethylarsine reacts very readily with cyanogen bromide in dry ethereal solution, yielding an insoluble precipitate in which the presence of nitrogen can occasionally be established, but which is at once converted on exposure to air (during filtration) into *triethylarsine hydroxybromide*, $AsEt_3Br{\cdot}OH$, colourless needles, m. p. 149—150°. Obviously, there is an intermediate formation of *triethylarsine bromocyanide* which, like the corresponding dihalogenides, but in an even more marked degree, readily undergoes hydrolysis; the isolation of the compound, m. p. 67°, has been effected by mixing the specially-dried components in light petroleum (b. p. 40—55°) solution in the apparatus designed by Wolfram (this vol., ii, 395). Apart from its susceptibility to moisture, it is a stable, crystalline substance. It differs from the corresponding compounds formed from tertiary amines, not only in its ready hydrolysis, but also in the relative difficulty with which it can be caused to eliminate ethyl bromide; this can be effected by heating it in a vacuum, whereby *diethylcyanoarsine*, $AsEt_2{\cdot}CN$, a colourless liquid with the typical odour of cacodyl compounds, b. p. 74°/12 mm., and m. p. about 50°, is obtained smoothly. H. W.

Organic Derivatives of Silicon. XXIV. *dl*-Derivatives of Silicoethane. FREDERICK STANLEY KIPPING (T., 1921, **119**, 647—653).

Organo-derivatives of Thallium. I. Some Reactions of Thalliumdialkyl Haloids. ARCHIBALD EDWIN GODDARD (T., 1921, **119**, 672—676).

Interaction of Acetylene and Mercuric Chloride. II. WILLIAM JOB JENKINS (T., 1921, **119**, 747—749).

Ethylstannic Acid and Derivatives. JOHN GERALD FREDERICK DRUCE (T., 1921, **119**, 758—763).

Decomposition of Hydrocarbons by Canal Rays. V. KOHLSCHÜTTER and A. FRUMKIN (*Ber.*, 1921, **54**, [*B*], 587—594).—The vapours of naphthalene, benzene, diphenyl, anthracene, phenanthrene, fluorene, decane, and petroleum have been subjected to the action of canal rays in a vessel so designed that they can be passed at a desired pressure between an anode of aluminium wire and a specially constructed cylindrical cathode. In every case, the latter becomes more or less rapidly coated with a deposit which ultimately is of sufficient thickness to impede the passage of the current and stop the experiment. The properties of the deposits depend on the potential of the cathode and not on the mode of union of the carbon in the decomposed substance. With low potentials (200—400 volts), they are transparent and coherent; when heated, they evolve large amounts of gas and tar, leaving a coherent deposit of brown coal on the cathode. With potentials of 500—700 volts, the layers are darker in colour and exhibit crevices; they evolve less gas and tar when heated, and become semi-fused. The deposits with potentials of 700—1500 volts are black and inclined to scale off; they do not yield tar when heated, and only a little gas. With still higher potentials (2000—5000 volts), the deposits consist of almost pure carbon in loose layers, from which practically no gas is evolved even after intense ignition. The carbon obtained directly, or after ignition of the deposits, resembles anthracite in properties and differs both chemically and physically from graphite or retort carbon; this is the more remarkable in the former case, since the effect of the atomic bombardment must correspond with that of an extremely high temperature. H. W.

The Three Tetrachlorobenzenes. A. F. HOLLEMAN (*Rec. trav. chim.*, 1921, **40**, 318—319).—An addendum to previous work (this vol., i, 103). Further proof is given that the accessory product obtained in the action of sodium methoxide on pentachlorobenzene is 2 : 3 : 4 : 5-tetrachlorophenol. W. G.

Styrene from Ethylbenzene. JULIUS VON BRAUN and KARL MOLDÄNKE (*Ber.*, 1921, **54**, [*B*], 618—619).—Styrene may be obtained in good yield from ethylbenzene by direct bromination of the latter to $\alpha\beta$-dibromoethylbenzene, b. p. 133°/19 mm., m. p. 72° and treatment of the bromo-derivative with metallic magnesium. Small quantities of the so-called "liquid distyrene" appear to be also formed, but these do not influence the isolation of the main product. Dibromoethylbenzene reacts vigorously with zinc when

dissolved in ether or acetone; the product of the reaction consists of highly polymerised styrene containing only minimal quantities of styrene itself. The observations are similar to those made with αβ-dibromotetrahydronaphthalene (von Braun and Kirschbaum, next page). H. W.

Preparation of Reduction Products of Nitrotetrahydronaphthalenes. TETRALIN G. M. B. H., Berlin (D.R.-P. 333157; from *Chem. Zentr.*, 1921, ii, 737—738).—Nitro-compounds obtained by the nitration of tetrahydronaphthalene and its homologues are subjected to reduction by ordinary methods. All intermediate compounds between the nitro-derivatives and amines are obtained. The aryl-amino-derivatives can be used in the preparation of dyes. By reduction of a mixture of 1- and 2-nitrotetrahydronaphthalene, a mixture of the corresponding *ar*-amino-compounds is obtained which can be separated by fractional crystallisation of the hydrochlorides, or by way of the easily prepared acetyl derivatives. 1-*Acetylaminotetrahydronaphthalene* melts at 156—158°, 2-*acetylaminotetrahydronaphthalene* at 105—106°. 1-*Aminotetrahydronaphthalene* is a colourless liquid when freshly distilled, becoming red on exposure to light and air; does not solidify on cooling with ice; b. p. 146°/12 mm., and may be distilled without decomposition at ordinary pressure. 2-*Aminotetrahydronaphthalene* forms colourless crystals, m. p. 38·5—39·5°, b. p. 146—147°/12 mm. By partial reduction of the mixture of the two nitro-compounds, the 2-nitro-compound is completely, and the 1-nitro-compound partly, changed into the corresponding amines. By shaking with hydrochloric acid, the pure 1-nitrotetrahydronaphthalene remains. This gives, by reduction with the proper amount of zinc dust and sodium hydroxide in dilute alcoholic solution, 1-*azotetrahydronaphthalene*, ruby-red prisms, m. p. 175—177°. By further reduction, 1-*hydrazotetrahydronaphthalene* is obtained as long, shining, colourless needles from glacial acetic acid and ether, m. p. 180—182°, with partial conversion into azotetrahydronaphthalene in the form of a red liquid. 1-Hydrazotetrahydronaphthalene is stable in air, but is easily oxidised to the azo-compound: with mineral acids it gives 4 : 4′-*diamino*-1 : 1′-*octahydrodinaphthyl*. Reduction of 1 : 3-*dinitrotetrahydronaphthalene* dissolved in boiling alcohol and ethyl acetate gives a *nitroamine* of tetrahydronaphthalene, orange-yellow crystals, m. p. 94—96°. As it agrees with the product obtained by the nitration of 2-acetylaminotetrahydronaphthalene, it must be 4-*nitro*-2-*aminotetrahydronaphthalene*. By complete reduction, 1 : 3-*diaminotetrahydronaphthalene* is obtained as a yellow oil, solidifying on cooling, m. p. 72—74°, b. p. above 201—203°/13 mm. The *benzoyl* derivative has m. p. 235°, and the *benzylidene* derivative, m. p. 208°. Reduction of 3-*nitro*-2-*aminotetrahydronaphthalene* gives 2 : 3-*diaminotetrahydronaphthalene*, colourless crystals, m. p. 135—136°; this gives on boiling with glacial acetic acid a *glyoxaline*, $C_{10}H_{10}<{\overset{N}{\underset{NH}{}}}>CMe$, m. p. 251—252°. G. W. R.

Benzo-polymethylene Compounds. II. Brominated Alicyclic Substitution Products of Tetrahydronaphthalene and Δ^1-Dihydronaphthalene. JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1921, **54**, [*B*], 597—618. Compare A., 1920. i, 618).—Tetrahydronaphthalene scarcely reacts with bromine in the dark and in the absence of a catalyst, but in the presence of iron, or preferably of iodine, the benzenoid nucleus is readily brominated; at a higher temperature or under the influence of light, the hydrogenated ring is attacked with ease, but, unexpectedly, the only isolable product appears to be $\alpha\beta$-dibromotetrahydronaphthalene, which is formed independently of the relative proportions of the reagents.

ac-$\alpha\beta$-Dibromotetrahydronaphthalene, colourless crystals, m. p. 70° (compare Straus and Lemmel, A., 1913, i, 256), is readily prepared by the addition of bromine to tetrahydronaphthalene heated on the boiling water-bath; it distils without sensible decomposition at 165—173°/12 mm., but the minimal amounts of impurity thus introduced so greatly retard the subsequent crystallisation that it is preferable to avoid distillation during the preparation. It is scarcely affected by trimethylamine, dimethylaniline, or pyridine at 100°, whilst primary and secondary aromatic amines convert it into nitrogenous, polymolecular products; a molecule of hydrogen bromide can, however, be removed under the influence of diethylamine or pyridine, whereby an apparently homogeneous *bromo-Δ^1-dihydronaphthalene*, b. p. 137°/15 mm., is obtained (*dibromide*, $C_{10}H_9Br_3$, leaflets, m. p. 71°), the constitution of which has not been further elucidated, since it was not found possible to effect reduction at the double bond without at the same time removing the bromine atom.

The action of zinc and alcohol on $\alpha\beta$-dibromotetrahydronaphthalene (compare Willstätter and King, A., 1913, i, 353; Straus, A., 1913, i, 455) under the most favourable conditions does not yield more than 80% of Δ^1-dihydronaphthalene, the remainder appearing to consist of a mixture of hydrocarbons from which an individual substance could not be isolated. A much more energetic reaction occurs when the alcohol is replaced by a hydroxyl-free solvent such as benzene, ether, or acetone, and from these experiments it has been found possible to isolate a *polymeride* of Δ^1-dihydronaphthalene $(C_{10}H_{10})_8$, yellow powder, m. p. 220°, after slight softening at 212°, which appears to owe its production to the intermediate formation of organo-metallic complexes. In contrast to styrene, Δ^1-dihydronaphthalene appears to be unaffected by protracted exposure to light or repeated distillation. When diluted with a hydrocarbon (light petroleum, benzene, xylene, tetrahydronaphthalene) and treated with concentrated sulphuric acid, however, it yields bis-Δ^1-dihydronaphthalene, b. p. 243—245°/12 mm., in excellent yield, from which, after protracted cooling, a crystalline *product*, $C_{20}H_{20}$, m. p. 93°, separates. Dehydrogenation of the separated products with lead oxide shows that the latter yields *bisnaphthylene*, yellow powder, m. p. 165°, in much the greater amount, thus making it probable that the original oil is a mixture

of isomerides. The constitution of the products has not been fully elucidated, but oxidation of them is found to give phthalic and phthalonic acids. The possibility that Δ^1-dihydronaphthalene, like styrene, might combine with the aromatic hydrocarbon during the course of the polymerisation experiments is also considered, but is rejected, since it is found that the *substance* derived from tetrahydronaphthalene and styrene has b. p. 221—225°/22 mm.

Δ^1-Dihydronaphthalene, b. p. 91°/15 mm., m. p. −8°, $D_4^{21.5}$ 0·9963, is very readily and quantitatively produced by the action of magnesium on dibromotetrahydronaphthalene in the presence of ether; the latter need not be dry, but must be completely freed from alcohol.

One of the bromine atoms of dibromotetrahydronaphthalene is readily replaceable. Thus when the substance is heated with aqueous acetone it gives ac-β-*bromo*-α-*hydroxytetrahydronaphthalene*, colourless crystals, m. p. 112°. The following products are prepared by heating it with the requisite alcohol: ac-β-*bromo*-α-*methoxytetrahydronaphthalene*, colourless liquid, b. p. 151—152°/13 mm.; ac-β-*bromo*-α-*ethoxytetrahydronaphthalene*, b. p. 171—172°/21 mm.; ac-β-*bromo*-α-*amyloxytetrahydronaphthalene*, b. p. 175—180°/15 mm.; ac-β-*bromo*-α-*allyloxytetrahydronaphthalene*, b. p. 171°/11 mm. (the corresponding *dibromide* is an oil). The bromoalkyloxytetrahydronaphthalenes all become decomposed slightly when preserved. The β-position of the bromine atom in the foregoing compounds is demonstrated by the conversion of the ethoxy-compound into ββ-dinaphthyl. This is effected by means of magnesium, which yields primarily a mixture of α-*ethoxytetrahydronaphthalene* and αα′-*diethoxy*-ββ′-*bistetrahydronaphthalene*; neither ether could be isolated in the pure condition by reason of the ready elimination of ethyl alcohol with formation of Δ^1-*dihydronaphthalene* and *bis*-Δ^1-*dihydronaphthalene*, colourless leaflets, m. p. 156° (the conversion can be made quantitative in either case by boiling the crude product with dilute sulphuric acid). *Bis*-Δ^1-*dihydronaphthalene* is readily reduced by sodium and ethyl alcohol to ββ′-*bistetrahydronaphthalene*, colourless leaflets, m. p. 113°, from which ββ′-dinaphthyl is obtained by distillation over lead oxide. The latter substance is also readily obtained by the bromination of bis-Δ^1-dihydronaphthalene, since the primary tetrabromide readily loses hydrogen bromide. Attempts to reduce the β-bromo-α-alkyloxytetrahydronaphthalenes to the halogen-free ethers were unsuccessful. β-*Bromo*-α-*acetoxytetrahydronaphthalene*, colourless, shining needles, m. p. 95—96°, is readily obtained by the continuous action of potassium acetate and glacial acetic acid on dibromotetrahydronaphthalene, and is converted by alcohol and fuming hydrochloric acid at 50—60° into β-bromo-α-hydroxytetrahydronaphthalene.

Tetrahydronaphthalene reacts readily with chlorine at 100°, yielding apparently αβ-*dichlorotetrahydronaphthalene*, b. p. 155—160°/20 mm.; the product, however, persistently retains small quantities of impurity, which cannot be removed by repeated fractional distillation. Its constitution follows from its conversion into Δ^1-dihydronaphthalene in good yield by zinc and alcohol, but

it is less suited for the preparation of this substance than is αβ-dibromotetrahydronaphthalene. H. W.

Exhaustive Sulphonation of Naphthalene. HANS EDUARD FIERZ and FRITZ SCHMID (*Helv. Chim. Acta*, 1921, 4, 381—387).—The investigations of Armstrong and Wynne (P., 1885 to 1895) showed that sulphonic groups never enter the naphthalene nucleus in the ortho-, para-, or peri-position to one another. According to this rule, exhaustive sulphonation of naphthalene can lead to only two end products, namely, naphthalene-1 : 3 : 6-trisulphonic and 1 : 3 : 5 : 7-tetrasulphonic acids. It has, however, been stated [D.R.-P. 79054 (By)] that these two acids are accompanied by Senhofer's naphthalenetetrasulphonic acid (A., 1882, 624) when naphthalene is heated at 260° with concentrated sulphuric acid and phosphoric oxide; the authors find that this statement is inaccurate.

It is found, further, that barium naphthalene-1 : 3 : 5 : 7-tetrasulphonate is dimorphous, the transformation point being about 30°. Above this temperature, the salt crystallises with $8H_2O$ and below it with $14H_2O$; both salts give one and the same tetrasulphochloride, m. p. 261—262°. The 1 : 3 : 5 : 7-tetrasulphonic acid is formed with great readiness, and is perfectly inactive towards nitric acid. The apparent losses encountered in the manufacture of H-acid are dependent on the formation of the tetrasulphonic acid and on oxidative destruction of naphthalene. Together with the tetrasulphonic acid, the 2 : 7- and the 1 : 6-disulphonic acids are often formed in small proportions, so that these two acids undergo further sulphonation to the 1 : 3 : 6-trisulphonic acid only with difficulty. 1-Nitronaphthalene-3 : 6 : 8-trisulphonic acid, which is accompanied by no isomeride in detectable amount, has been isolated and characterised; its dissociation constant has the value 0·095 (compare Fierz and Weissenbach, A., 1920, i, 429). The *lead*, $Pb_3[C_{10}H_4(NO_2)(SO_3)_3]_2,8H_2O$, *barium* ($8H_2O$), *sodium* ($6H_2O$), and *aniline* salts ($2\frac{1}{2}H_2O$) of the acid were prepared and analysed. T. H. P.

Synthesis of Anthracene from Naphthalene. C. W. COLVER and WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 898—905).—An unsuccessful attempt to synthesise anthracene from a derivative of naphthalene in which the actual nucleus of the naphthalene molecule was known to remain intact.

Attempts to condense 2 : 3-dibromotetrahydronaphthalene with malonic ester in the presence of sodium or magnesium ethoxides were not successful. Ethyl Δ^2-dihydro-β-naphthoate condensed with ethyl acetoacetate in the presence of sodium ethoxide to give *ethyl* 2 : 4-*diketo-octahydroanthracene*-1-*carboxylate*, which when hydrolysed gave the free *acid*. The acid when heated on a water-bath lost carbon dioxide, yielding 2 : 4-diketo-octahydroanthracene, which on distillation with zinc dust gave anthracene. W. G.

Preparation of Polycyclic Hydroaromatic Hydrocarbons. TETRALIN G. M. B. H., Berlin (D.R.-P. 333158; from *Chem. Zentr.*, 1921, ii, 739).—Tetrahydronaphthalene is treated with a much less

than molecular proportion of aluminium chloride at temperatures up to 100°. The principal products are octahydroanthracene and octahydrophenanthrene, according to the equation, $4C_{10}H_{12}=2C_6H_6+2C_{14}H_{18}$. By long-continued action, compounds of higher molecular weight containing more condensed nuclei are obtained. For example, 1000 parts of tetrahydronaphthalene are treated with 15 to 20 parts of aluminium chloride for six hours at a temperature below 100°. The liquid product, freed from a dark brown sediment, and washed with acidified water, is fractionated. The first fractions are benzene and tetrahydronaphthalene. At 160—170°/11 mm., the greater part of the *octahydrophenanthrene* distils over; octahydroanthracene following at 170—180°/11 mm. The former is an oil of low freezing point, giving phenanthrene when heated with sulphur or distilled with zinc dust. *Octahydroanthracene* crystallises from the fraction 160—170° in colourless plates, m. p. 72—73°. It is not identical with the octahydroanthracene melting at 71° described by Godchot (A., 1904, i, 987; A., 1905, i, 201, and A., 1907, i, 308), since it does not give a picrate, shows no green fluorescence, and does not sublime easily. When heated with sulphur or distilled with zinc dust, anthracene is formed. Above 230°/11 mm., other polycyclic compounds distil over. These also can be dehydrogenated by sulphur. For example, the hydroaromatic hydrocarbon from the fraction 233—235°/12 mm. yields an aromatic *hydrocarbon*, boiling without decomposition, prisms, m. p. 168—169°, from alcohol. These products can be used as lubricants. Octahydroanthracene and octahydrophenanthrene can be nitrated, sulphonated, and halogenated for the preparation of dyes, drugs, and perfumes. G. W. R.

Aniline Lead Compounds. HJ. MANDAL (*Ber.*, 1921, **54**, [*B*], 703—708).—An extension of previous observations (this vol., i, 106) to compounds of lead.

Lead fluoride, sulphate, phosphate, and nitrate do not appear to react with aniline to an appreciable extent. Simple and double compounds are, however, derived from the lead haloids. The compounds are prepared by warming the haloid or mixture of haloids with aniline and allowing the saturated solution to crystallise at the ordinary temperature. They are unstable substances, readily decomposed by water, alcohol, ether, etc. The following individuals are described: *trianiline lead chloride*, $PbCl_2,3NH_2Ph$, colourless, matted needles, D^{18} 1·98, which gradually lose the whole of the base at 20—22°, particularly on exposure to light: *dianiline lead bromide*, colourless needles, D^{17} 2·47, which lose aniline at 20—22°, and ultimately leave a residue of the *compound*, $3PbBr_2,2NH_2Ph$: *aniline lead iodide*, shining yellow needles, D^{18} 3·80, which retain the base more firmly than the compounds just described: the *compound*, $PbBr_2,3PbCl_2,12NH_2Ph$, slender, colourless, lustrous needles: *compound*, $PbI_2,6PbBr_2,14NH_2Ph$, very pale yellow needles, which are transformed by alcohol into the bright yellow *substance*, $PbI_2,6PbBr_2,4NH_2Ph$: *compound*, $PbI_2,3PbBr_2,8NH_2Ph$ (from the components in boiling solution), very pale yellow needles which,

with alcohol, yield the yellow *substance*, $PbI_2,3PbBr_2,2NH_2Ph$. Mixed compounds containing lead chloride and iodide could not be prepared. H. W.

Ethers Derived from the Additive Products of the Nitroanilines and Chloral. ALVIN S. WHEELER and SAMUEL C. SMITH (*J. Amer. Chem. Soc.*, 1921, **43**, 941—945. Compare A., 1920, i, 93).—If *m*-nitroaniline and chloral in equimolecular quantities are mixed directly or in ethereal solution, a gummy substance is produced, which if heated for several hours is converted into a crystalline condensation *compound*, $CCl_3·CH(NH·C_6H_4·NO_2)_2$, m. p. 130°. If, however, the gummy mass is dissolved in hot alcohol, an ether is obtained. Similar results are obtained with other alcohols, and the following compounds are described : N-(β-*trichloro*-α-*methoxyethyl*)-m-*nitroaniline*, $CCl_3·CH(OMe)·NH·C_6H_4·NO_2$, m. p. 108—109° ; N-(β-*trichloro*-α-*ethoxyethyl*)-m-*nitroaniline*, m. p. 90° ; N-(β-*trichloro*-α-*propoxyethyl*)-m-*nitroaniline* ; N-(β-*trichloro*-α-*butoxyethyl*)-m-*nitroaniline*, m. p. 70°, and N-(β-*trichloro*-α-iso*amyloxyethyl*)-m-*nitroaniline*, m. p. 90°.

Only two such ethers could be obtained from *p*-nitroaniline and chloral, namely : N-(β-*trichloro*-α-*methoxyethyl*)-p-*nitroaniline*, m. p. 146—147°, and N-(β-*trichloro*-α-*ethoxyethyl*)-p-*nitroaniline*, m. p. 138°. These were best prepared by the interaction of *p*-nitroaniline and the chloral alcoholate. W. G.

The Addition of Aromatic Amines to Bromonitrostyrene. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1921, **43**, 919—925).—Further evidence is given in support of the view that bromonitrostyrene as first prepared by Priebs (A., 1884, 313) has the constitution $CHPh\!:\!CBr·NO_2$, assigned to it by Thiele (A., 1903, i, 160). It reacts with *p*-toluidine to form an additive compound, α-*bromo*-α-*nitro*-β-p-*toluidino*-β-*phenylethane*, $C_6H_4Me·NH·CHPh·CHBr·NO_2$, m. p. 107—108° (decomp.), which is decomposed by heat, giving bromonitromethane and *p*-tolylbenzylideneamine. When heated with hydrochloric acid this additive compound is rapidly decomposed, giving benzaldehyde, bromonitromethane, and *p*-toluidine hydrochloride, but if dry hydrogen chloride is passed into its ethereal solution it yields its own *hydrochloride*, m. p. 102—104° (decomp.). With cold aqueous sodium hydroxide, bromonitrotoluidinophenylethane gives a *sodium* salt, but on warming with the alkali it is decomposed, and amongst the products benzaldehyde and hydrobenzoin were detected. With bromine in chloroform solution, the toluidinoethane is decomposed, giving 3 : 5-dibromo-*p*-toluidine, bromonitromethane, benzaldehyde, and bromonitrostyrene. On nitration, it gave a *dinitro*-derivative, m. p. 154—155°, the nitro-groups being in the toluidine radical.

With phenylhydrazine in cold alcoholic solution, bromonitrostyrene yielded α-*bromo*-α-*nitro*-β-*phenylhydrazino*-β-*phenylethane*, $NHPh·NH·CHPh·CHBr·NO_2$, m. p. 83—83·5°, which reacts with bromine, forms a *salt* with hydrogen chloride, and is easily decomposed, giving phenylbenzylidenehydrazine and bromonitromethane.

The additive compounds formed with bromonitrostyrene and

aromatic amines and hydrazines decomposed as fast as they were formed into bromonitromethane and Schiff's bases, the latter being further decomposed by bromonitromethane into benzaldehyde and amine. Substituted aromatic amines containing negative groups did not react with bromonitrostyrene. W. G.

Some Properties of Nitroamines and their Derivatives. F. M. ROWE (*J. Soc. Dyers and Col.*, 1921, **37**, 145—150).—A collection and review of the author's work on nitroamines which has been already published (T., 1912, **101**, 2003, 2443, 2452; 1913, **103**, 508, 897, 2023; 1917, **111**, 612; 1918, **113**, 67; 1920, **117**, 1344). F. M. R.

Thermal Decomposition of Phenoxides. FRANZ FISCHER and UDO EHRHARDT (*Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 237—263; from *Chem. Zentr.*, 1921, i, 762—763).—Potassium and sodium phenoxides behave exceptionally in that when dry they give only gaseous products, hydrogen, and a little methane; they decompose at 450—500°. Sodium phenoxide, when heated in a current of carbon dioxide, gives hydrogen and carbon monoxide as well as liquid products. Decomposition in a stream of carbon monoxide gives methane, small quantities of phenol, and benzene. Fusion of sodium phenoxide with sodium formate at red heat gives a red liquid distillate as well as benzene. Fusion of sodium phenoxide with sodium hydroxide and carbon gives only traces of phenol. *Lithium phenoxide* decomposes at 450°, giving liquid products as well as hydrogen, methane, and carbon monoxide and dioxide. *Normal calcium phenoxide* gives principally phenol. *Basic calcium phenoxide*, OH·Ca·OPh, decomposes at 450°, giving liquid products as well as hydrogen, methane, and carbon monoxide. Decomposition in a stream of carbon dioxide gives complete decomposition into calcium carbonate and phenol. *Barium phenoxide* decomposes at 600°, giving a small amount of liquid products with hydrogen, methane, and carbon monoxide. *Aluminium phenoxide* decomposes below a red heat, giving liquid products (benzene, phenol, diphenyl ether, methyl diphenylene oxide, and pyrocresol), as well as hydrogen and methane. Phenoxides of magnesium, zinc, and iron could not be prepared. *Basic copper phenoxide*, OH·Cu·OPh, prepared from copper sulphate and potassium phenoxide, gave no noteworthy decomposition products. It was shown that phenol with concentrated ammonia in the presence of copper is oxidised by air, giving a deep black solution which becomes viscous on evaporation, solidifying to a varnish-like product. *Basic nickel phenoxide*, OH·Ni·OPh, decomposes below a red heat, giving a small quantity of liquid product as well as carbon dioxide, carbon monoxide, hydrogen, and methane. *Basic lead phenoxide*, OH·Pb·OPh, decomposes below a red heat giving liquid products (phenol, diphenylene oxide, and a reddish-brown oil) and carbon dioxide. Heated somewhat above 100°, it fuses and solidifies to a glassy substance on cooling.

Sodium p-*tolyloxide*, prepared by the action of sodium or sodium hydroxide on *p*-cresol, decomposes between 450° and 600°. More

methane is formed than in the case of the phenoxide, and large quantities of liquid products are obtained, consisting chiefly of cresol. *Sodium* m-*tolyloxide* decomposes in a similar manner. *Potassium* p-*tolyloxide* decomposes between 420° and 550° similarly to sodium phenoxide. *Basic calcium* p-*tolyloxide*, $OH\cdot Ca\cdot O\cdot C_7H_7$, gives, on dry distillation, mainly cresol. G. W. R.

Preparation of Derivatives of *p*-Aminophenol and of its *o*-Alkyl Ethers. ERICH KOLSHORN (Brit. Pats. 145614, 155575, 155576).—Compounds soluble in water are obtained by converting *p*-aminophenol and its O-alkyl ethers into N-dihydroxypropyl derivatives of the general formula $OR\cdot C_6H_4\cdot NH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$. These derivatives are obtained by causing the amines to react either directly, or in a neutral solvent, with monochlorohydrin or with epihydrin alcohol (glycide). Thus 22 grams of *p*-aminophenol when gently heated with 15 grams of glycide in benzene solution is converted into N-*dihydroxypropyl*-p-*aminophenol*, m. p. 192°, readily soluble in water, giving a solution which has a powerful reducing action on silver salts and is specially suitable as a photographic developer. N-*Dihydroxypropyl*-p-*anisidine*, m. p. 75—76°, is obtained in a similar way. N-*Dihydroxypropyl*-p-*phenetidine* may be obtained from *p*-phenetidine (14 parts) by the action of α-monochlorohydrin (11 parts) in presence of cold 20% alcoholic potassium hydroxide. It melts at 93°, is readily soluble in water, and has valuable therapeutic properties. The above dihydroxypropyl derivatives can also be obtained by condensing the amines with epichlorohydrin with or without the addition of a neutral solvent, and treating the chloro-compound, $OR\cdot C_6H_4\cdot NH\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$, thus produced, with the theoretical amount of alcoholic potassium hydroxide, or alternatively, the amines may be brought into reaction in the cold with α-α- or α-β-dichlorohydrin in presence of alcoholic alkali hydroxide, or pyridine, whereby hydrogen chloride is eliminated and the same chloro-intermediate product produced as above, which, on warming with a further quantity of alcoholic alkali hydroxide, is converted into the dihydroxypropyl derivative required. G. F. M.

Formation of Nitrophenetole from Chloronitrobenzene. A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 297—318).—When an alcoholic solution of *o*- or *p*-chloronitrobenzene is heated in a reflux apparatus with an equivalent proportion of potassium hydroxide solution, the reactions occurring are principally as follows: $NO_2\cdot C_6H_4Cl + KOR \longrightarrow$ either $NO_2\cdot C_6H_4\cdot OR$ (I) or $NO_2\cdot C_6H_4\cdot OH$ (II) or $O<\begin{matrix} N\cdot C_6H_4Cl \\ | \\ N\cdot C_6H_4Cl \end{matrix}$ (III). These reactions have been followed by estimating ionic chlorine by titration with silver nitrate solution (Ag-titre), and by titrating the solution with standard acid solution in presence of either phenolphthalein (Ph-titre) or Congo-red (Ko-titre); the Ag-titre corresponds with reactions I and II, the Ko-titre with reactions I and III, the Ph-titre with reactions I, II, and III, the sum of the Ph- and Ag-titres with reaction III, and the excess

of the Ko-titre over the Ph-titre with reaction II. The course of each separate reaction may, therefore, be traced, and information obtained concerning the influence exerted by the temperature, the solvent, the nature of the alkali employed, etc. The factors leading to enhanced yields of the *p*- or *o*-nitrophenetole are also indicated by the results, as well as those favouring the suppression of the dichloroazoxybenzene, which is industrially valueless. The kinetics of the reactions are considered. T. H. P.

Lichen Products. III. Determination of the Constitution of Divarinol. ADOLF SONN (*Ber.*, 1921, **54**, [*B*], 773—774. Compare A., 1917, i, 143).—Hesse has isolated divarinol, m. p. 82—83°, from various species of *Evernea* and has considered it to be 3 : 5-dihydroxy-1-*n*-propylbenzene. Since 2 : 4-dihydroxy-1-*n*-propylbenzene (Johnson and Hodge, A., 1913, i, 1055) has the same melting point, it appeared possible that the two substances might in reality be identical. Repetition of the latter work, however, has shown that anhydrous 2 : 4-dihydroxy-1-*n*-propylbenzene has m. p. 107—108°, b. p. 172—174°/14—15 mm., whilst the hydrated form has m. p. 71°; the product obtained by Johnson and Hodge appears to have been incompletely freed from water of crystallisation, which is very obstinately retained.

Introduction of the aldehydic group into 2 : 4-dihydroxy-1-*n*-propylbenzene by Gattermann's method leads to the formation of 2 : 4-*dihydroxy*-5-n-*propylbenzylideneaniline*, $C_6H_2Pr(OH)_2{\cdot}CH{:}NPh$, coarse, greenish-yellow prisms, m. p. 159° (decomp.), which is hydrolysed to 2 : 4-*dihydroxy*-5-n-*propylbenzaldehyde*, plates, m. p. 71—76°, which was not isolated in a perfectly homogeneous condition. H. W.

The Valency Problem of Sulphur. IV. Arylthiol Thiocyanates. HANS LECHER and KURT SIMON (*Ber.*, 1921, **54**, [*B*], 632—638).—The investigation deals with the possibility that compounds of the type, ArS·SCN, may belong to the class of arylcyanodisulphides with homopolar union, and may thus be expected to show the halogen-like reaction of free thiocyanogen (compare Söderbäck, A., 1920, i, 219), or may be sulphur aryl thiocyanates with heteropolar union of the sulphur atoms, in which case they should show close analogy with the arylthiol chlorides. It is found that sulphur *o*-nitrophenyl thiocyanate, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}C{:}N$, very nearly resembles *o*-nitrochlorothiolbenzene, $NO_2{\cdot}C_6H_4{\cdot}SCl$ (Zincke and Farr, A., 1912, i, 763).

o-*Nitrophenylthiol thiocyanate*, yellow crystals, m. p. 93—94°, is obtained by the action of potassium thiocyanate on *o*-nitrochlorothiolbenzene or of free thiocyanogen on *o*-nitrophenyl mercaptan. Its adherence to the thiocyanogen series is shown by its transformation by ammonia into *o*-nitrophenylthiolamine, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}NH_2$, m. p. 124—125° (decomp.). The substance behaves towards alcoholic potassium hydroxide solution, dimethylaniline, and thiophenol respectively in precisely the same manner as *o*-nitrochlorothiolbenzene (Zincke and Farr, *loc. cit.*). The strict proof of the ionisable nature of the compound cannot, however, be given, since its solution

in liquid sulphur dioxide is a non-conductor. In one particular the chloride and thiocyanate exhibit marked difference in behaviour, since the latter is practically unaffected by water (and is quite insensitive to atmospheric moisture) under conditions which cause the ready hydrolysis of the former to hydrochloric acid and the oxide. The same difference is shown by triphenylmethyl thiocyanate and chloride. The former forms colourless, shining crystals, m. p. 137°, b. p. 203°/4 mm., and, contrary to the data of Elbs, is not stable towards heat. It is absolutely unaffected by water at the atmospheric temperature, and is unchanged by ammonia at 80°. H. W.

Synthesis of Chlorine-free Benzoic Acid from Benzene. RALPH H. MCKEE and FRANK A. STRAUSS (*Chem. and Met. Eng.*, 1921, **24**, 638—644, 697—702).—The reactions involved in the conversion of sodium benzenesulphonate into benzoic acid were investigated with a view to their utilisation on a commercial scale. Experiments on the direct formate fusion method indicated that benzoate formation takes place only at a high temperature and is accompanied by much decomposition, and this synthesis has therefore no practical value. Synthesis through benzonitrile gave greater promise of success on the technical scale. The main reaction in which benzonitrile is formed is accompanied by side reactions of two general types: reduction of the sodium benzenesulphonate by sodium cyanide and decomposition by water vapour of the sodium cyanate formed into sodium carbonate, carbon dioxide, and ammonia, and, secondly, pyrogenic decomposition of the benzenesulphonate with production of thio-ethers, thio-phenols, and hydrogen sulphide amongst numerous other by-products. The most favourable reaction conditions for the formation of the maximum yield of benzonitrile were shown to be: temperature of the reaction mixture between the narrow limits of 420° and 430°; finely powdered cyanide and sulphonate intimately mixed in equimolecular proportions, or a slight excess of cyanide; addition to the mixture of an inert diluent, for example, about 70% of its weight of sand. Under these conditions yields amounting to 43% of the theoretical were obtainable. Reduced pressure did not improve this result, but rather favoured the formation of sulphur compounds and tar. Hydrolysis of benzonitrile by sulphuric acid (D=1·6) was more rapid and efficient than alkali hydrolysis, and gave 95% yields of nearly pure benzoic acid. G. F. M.

The Preparation of Esters by Direct Replacement of Alkyloxy-groups. MARIE REIMER and HELEN RUPERT DOWNES (*J. Amer. Chem. Soc.*, 1921, **43**, 945—951. Compare A., 1911, i, 447; Pfannl, A., 1910, i, 480; 1911, i, 783).—It is found that in esters the alkyloxy-group may be directly replaced by another such group by leaving the ester in contact with the alcohol of which it is required to prepare the ester, provided that the alcohol contains a small amount of its potassium alkyloxide. Under these conditions, however, the reaction is restricted to primary alcohols. The conversion of methyl esters into those of higher primary alcohols and of ethyl into methyl esters, can be brought about with good yields, except in

the case of those acids which normally show " hindrance " to esterification, such as ortho-substituted esters. This method is of importance in the preparation of unstable esters which cannot be prepared at high temperatures or under the influence of acids. W. G.

[Preparation of] Allyl *p*-Aminobenzoate. R. ADAMS and E. H. VOLWILER (U.S. Pat. 1360994).—By heating a mixture of molecular proportions of *p*-nitrobenzoyl chloride with allyl alcohol under reflux for one to two hours, and fractionation in a vacuum, *allyl* p-*nitrobenzoate*, is obtained as a straw-coloured oil, b. p. 178°/19 mm. It is reduced with iron and hydrochloric acid at about 50°, filtered, made alkaline with sodium hydroxide, extracted with ether, the ethereal solution evaporated, and the *allyl* p-*aminobenzoate* crystallised from water or light petroleum; this melts at 51—52° and is a local anæsthetic.

Allyl 3 : 5-*dinitrobenzoate*, in the preparation of which excess of allyl alcohol is used, may be similarly reduced to *allyl* 3 : 5-*diaminobenzoate*, a viscous liquid which does not solidify at the ordinary temperature. It forms a yellow *dihydrochloride*, m. p. 224° (decomp.), when an ethereal solution is treated with excess of an alcoholic solution of hydrogen chloride. CHEMICAL ABSTRACTS.

Some Carbamido-acids and their Hydantoins. JOHN RICHARD SCOTT and JULIUS BEREND COHEN (T., 1921, **119**, 664—672).

The Application of Victor Meyer's Esterification Law to 2 : 6-Dimethylbenzoic Acid and its Reduced Derivatives. RALPH W. HUFFERD and WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 925—935).—The results obtained from a study of the esterification of 2 : 6-dimethylbenzoic acid and its reduction products, namely, 2 : 6-dimethyl-Δ^1-*cyclo*hexenecarboxylic acid, dimethyl-Δ^3-*cyclo*hexenecarboxylic acid, dimethyl-$\Delta^{1,5}$-*cyclo*hexadienecarboxylic acid, and *cyclo*hexanecarboxylic acid agree quite well with the predictions based on Victor Meyer's Esterification Law, but it is evident that the law cannot be applied quantitatively (compare Rosanoff, A., 1909, ii, 32).

In the reduction of 2 : 6-dimethylbenzoic acid by sodium in *iso*amyl alcohol both 2 : 6-*dimethyl*-Δ^3-cyclo*hexenecarboxylic acid*, m. p. 93·4°; n_D^{95} 1·4462; D^{95} 0·9553 and 2 : 6-dimethyl*cyclo*hexanecarboxylic acid, m. p. 75·5—75·8°; n_D^{85} 1·4371; D^{85} 0·9454, were obtained. The latter acid was cautiously treated with phosphorus pentachloride and after cooling and adding bromine the mixture was heated in a sealed tube. The resulting bromochloride was boiled in formic acid under a reflux condenser, and the bromo-acid which separated on cooling was boiled with alcoholic potassium hydroxide. On acidifying 2 : 6-dimethyl-Δ^1-*cyclo*hexenecarboxylic acid, m. p. 91—91·5°; n_D^{95} 1·4700; D^{95} 0·8625, was obtained. This acid on bromination gave 1 : 2-*dibromo*-2 : 6-*dimethyl*-Δ^1-cyclo*hexenecarboxylic acid*, m. p. 128—132° (decomp.), which, when treated with alkali, yielded 2 : 6-*dimethyl*-$\Delta^{1,5}$-cyclo*hexadienecarboxylic acid*, b. p. 155—160°/28 mm. The ionisation constants of these acids were determined by conductivity measurements. W. G.

The Relationship between Configuration and Physical Properties of the Esters of Halogenated Cinnamic Acids. K. VON AUWERS and E. SCHMELLENKAMP (*Ber.*, 1921, **54**, [*B*], 624—632).—The elucidation of the configuration of the cinnamic acids is frequently a matter of considerable difficulty, and this is particularly noticeable with the halogenated compounds. The only safe guide at present is Stoermer's rule that the boiling points of the methyl (and probably other) esters of the *cis*-acids is lower than that of the corresponding *trans*-forms (A., 1920, i, 613). In the hope of finding further regularities, the physical constants of the ethyl esters of a series of substituted cinnamic acids have been determined, but in no case is an absolutely uniform behaviour observed. On the other hand, a given compound does not show variations from the normal with respect to more than one constant, so that a fair guide is given by a consideration of a series of physical properties.

The requisite esters are conveniently prepared without danger of isomerisation by treating the acid with ethyl alcohol and sulphuric acid; the use of ethyl sulphate is inhibited by its slight reactivity and the action of ethyl iodide on the silver salt does not always proceed smoothly. The following constants are recorded: ethyl *trans*-α-chlorocinnamate, $D_4^{13\cdot4}$ 1·1823, $n_\alpha^{13\cdot4}$ 1·56903, $n_D^{13\cdot4}$ 1·57650, $n_\beta^{13\cdot4}$ 1·59801; ethyl *cis*-α-chlorocinnamate, $D_4^{12\cdot1}$ 1·1651, $n_\alpha^{12\cdot1}$ 1·54840, $n_D^{12\cdot1}$ 1·55440, $n_\beta^{12\cdot1}$ 1·57163, $n_\gamma^{12\cdot1}$ 1·58769; ethyl *trans*-α-bromocinnamate, $D_4^{14\cdot4}$ 1·4008, $n_\alpha^{14\cdot4}$ 1·58358, $n_D^{14\cdot4}$ 1·59114, $n_\beta^{14\cdot4}$ 1·61281, $n_\gamma^{14\cdot4}$ 1·63425; ethyl *cis*-α-bromocinnamate, $D_4^{12\cdot7}$ 1·3675, $n_\alpha^{12\cdot7}$ 1·56657, $n_D^{12\cdot7}$ 1·57310, $n_\beta^{12\cdot7}$ 1·59160; methyl *trans*-β-chlorocinnamate, $D_4^{21\cdot4}$ 1·2248, $n_\alpha^{21\cdot4}$ 1·57119, $n_D^{21\cdot4}$ 1·57810, $n_\beta^{21\cdot4}$ 1·59791, $n_\gamma^{21\cdot4}$ 1·61671; methyl *cis*-β-chlorocinnamate, $D_4^{26\cdot5}$ 1·1932, $n_\alpha^{26\cdot5}$ 1·54878, $n_D^{26\cdot5}$ 1·55457, $n_\beta^{26\cdot5}$ 1·57094, $n_\gamma^{26\cdot5}$ 1·58566; methyl *trans*-β-bromocinnamate, $D_4^{20\cdot2}$ 1·4520, $n_\alpha^{20\cdot2}$ 1·58636, $n_D^{20\cdot2}$ 1·59338, $n_\beta^{20\cdot2}$ 1·61319, $n_\gamma^{20\cdot2}$ 1·63175; methyl *cis*-β-bromocinnamate, $D_4^{70\cdot8}$ 1·3836, $n_\alpha^{70\cdot8}$ 1·55560, $n_D^{70\cdot8}$ 1·56124, $n_\beta^{70\cdot8}$ 1·57886; ethyl *trans*-β-bromocinnamate, $D_4^{10\cdot1}$ 1·4044, $n_\alpha^{10\cdot1}$ 1·57749, $n_D^{10\cdot1}$ 1·58405, $n_\beta^{10\cdot1}$ 1·60278, $n_\gamma^{10\cdot1}$ 1·61990; ethyl *cis*-β-bromocinnamate, $D_4^{10\cdot1}$ 1·3818, $n_\alpha^{10\cdot1}$ 1·56190, $n_D^{10\cdot1}$ 1·56761, $n_\beta^{10\cdot1}$ 1·58393, $n_\gamma^{10\cdot1}$ 1·59886; methyl *trans*-α-iodocinnamate, $D_4^{20\cdot5}$ 1·6679, $n_\alpha^{20\cdot5}$ 1·62427, $n_D^{20\cdot5}$ 1·63298, $n_\beta^{20\cdot5}$ 1·65783; methyl *trans*-αβ-dichlorocinnamate, D_4^{23} 1·3053, n_α^{23} 1·55640, n_D^{23} 1·56202, n_β^{23} 1·57762; methyl-*cis*-αβ-dichlorocinnamate, $D_4^{18\cdot75}$ 1·3042, $n_\alpha^{18\cdot75}$ 1·55871, $n_D^{18\cdot75}$ 1·56445, $n_\beta^{18\cdot75}$ 1·58055; methyl *trans*-αβ-dibromocinnamate, D_4^{75} 1·6607, n_α^{75} 1·56723, n_D^{75} 1·57295, n_β^{75} 1·58910; methyl *cis*-αβ-dibromocinnamate, $D_4^{20\cdot6}$ 1·7199, $n_\alpha^{20\cdot6}$ 1·59330, $n_D^{20\cdot6}$ 1·59965, $n_\beta^{20\cdot6}$ 1·61759. Ethyl *allo*-cinnamate has b. p. 125°/12 mm., $D_4^{11\cdot4}$ 1·0569, D_4^{20} 1·049, $n_\alpha^{11\cdot4}$ 1·54110, $n_D^{11\cdot4}$ 1·54833, $n_\beta^{11\cdot4}$ 1·56598, $n_\gamma^{11\cdot4}$ 1·58243, n_D^{20} 1·545. Ethyl cinnamate has b. p. 158·5—159°/24 mm., $D_4^{11\cdot4}$ 1·0566.

H. W.

The Preparation of *p*-Diphenylpropiolic Acid; and New Reactions of Diphenyl and its Derivatives. CHESTER L. KNOWLES (*J. Amer. Chem. Soc.*, 1921, **43**, 896—898).—Diazo-

benzene chloride is condensed with toluene by the method of Möhlau and Berger (A., 1893, i, 522, 701) and the resulting methyldiphenyl chlorinated directly. The resulting product without separating the mono- or tri-chloride also formed is heated in a sealed tube with water for four hours at 150°, and *diphenyl-4-aldehyde*, b. p. 121°, giving a *bisulphite* compound, is obtained. The aldehyde, when heated with potassium acetate and acetic anhydride, yields *diphenyl-4-acrylic acid*, m. p. 184°, giving an *ethyl* ester. This ester is brominated in solution in carbon tetrachloride and the product heated on a water-bath with potassium hydroxide, when *diphenyl-4-propiolic acid*, m. p. 147°, is obtained.

Attempts to condense *p*-diazocinnamic acid with benzene only yielded ββ-diphenylpropionic acid, m. p. 149°. W. G.

The Tolyl Cyanocampholates and their Product of Reduction. L. PALFRAY (*Compt. rend.*, 1921, **172**, 980—982).—The tolyl cyanocampholates may be obtained by heating the sodium derivatives of the three cresols, respectively, with cyanocamphor in a sealed tube for twenty-four hours at 200—220°. o-*Tolyl cyanocampholate* has m. p. 44—45°; b. p. 242—245°/14 mm.; m-*tolyl cyanocampholate* has m. p. 104—105°; b. p. 250°/25 mm.; and p-*tolyl cyanocampholate* has m. p. 119°; b. p. 248—250°/20 mm.; $[\alpha]_D^{21}$ +170° 32′. When reduced by sodium in absolute alcohol, *o*- and *p*-tolyl cyanocampholates yield *α-aminohomocampholyl alcohol*, $NH_2\cdot CH_2\cdot CH_2\cdot C_8H_{14}\cdot CH_2\cdot OH$, m. p. 76—77°; $[\alpha]_D^{21}$ +68° 43′, giving a *hydrochloride*, a *sulphate*, a *carbonate*, and a *platinichloride*.
W. G.

The Benzilic Acid Rearrangement. The Non-addition of Hydrogen Peroxide to Diphenylketen. BEN H. NICOLET and JOSEPH J. PELC (*J. Amer. Chem. Soc.*, 1921, **43**, 935—937).—Hydrogen peroxide does not react appreciably with diphenylketen in anhydrous solvents, even after eight months, nor does it react in the presence of water or alkali. These results are in opposition to Schroeter's explanation of the mechanism of the benzilic rearrangement (A., 1909, i, 617). W. G.

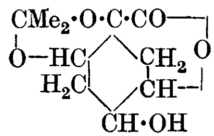
Preparation of Phthalic Anhydride. ALFRED WOHL (Brit. Pat. 145071).—When air or oxygen containing naphthalene vapours is passed over oxides of vanadium or other suitable catalyst distributed on pumice stone and heated at a temperature below 580°, preferably at 320—330°, oxidation to phthalic acid occurs and a white sublimate of pure phthalic anhydride can be directly obtained by suitable regulation of the velocity of the air mixture and of the proportion of naphthalene vapour. A suitable mixture is produced by passing air through or over naphthalene maintained at 100—120°. The catalyst is conveniently prepared by soaking pumice stone (18 parts) in a solution of 2 parts of vanadic acid, drying, and heating at about 320°. G. F. M.

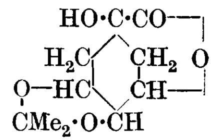
The Esterification of Dimethylamino*iso*phthalic Acid. I. Preparation of Methyl 4-Amino*iso*phthalate. N. SMODLAKA (*Rev. Chim.*, 1921, **1**, 71—74. Compare A., 1920, i, 737).—4-Acetyl-

amino*iso*phthalic acid, when treated with methyl alcohol and sulphuric acid, undergoes simultaneous de-acetylation and esterification, yielding methyl 4-amino*iso*phthalate (m. p. 131°) along with a small quantity of an acid by-product (m. p. 220°) which, apparently, is methyl hydrogen 4-amino*iso*phthalate. The yields throughout are good (compare Wegscheider, Malle, Ehrlich, and Skutzky, A., 1919, i, 76). C. K. I.

A Second Form of 6 : 6′-Dinitrodiphenic Acid, and its Conversion into New Cyclic Systems. JAMES KENNER and WILFRED VICTOR STUBBINGS (T., 1921, **119**, 593—602).

New Derivatives of Quinic Acid. HERMANN O. L. FISCHER (*Ber.*, 1921, **54**, [*B*], 775—784).—Tetra-acetylquinyl chloride, $C_6H_7O_4Ac_4$·COCl, microscopic prisms which soften at 104° and are completely molten at 122°, is prepared by the action of phosphorus pentachloride on a suspension of tetra-acetylquinic acid in chloroform; it is converted by methyl alcohol into the *methyl* ester and by aniline into the *anilide*, m. p. 211—212° (corr.). When dissolved in acetone and mixed with a well-cooled solution of sodium azide in water, it yields *tetra-acetylquinazide*, $C_6H_7O_4Ac_4$·CO·N_3, decomp. 93—95°, which is transformed in hot toluene solution into nitrogen, carbon dioxide, acetic acid, and 4-acetamidoacetoxybenzene, prismatic needles, m. p. 150—151°. Dry quinic acid is gradually converted at the atmospheric temperature by a 1% solution of hydrogen chloride in dry acetone into iso*propylidenequinide* (annexed formula I or II), slender needles, m. p. 140—141°, $[\alpha]_D^{18}$ −36·65° in *s*-tetrachloroethane solution.


(I.)


(II.)

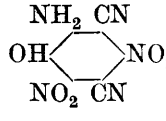
[With GERDA ANGER].—*iso*-Propylidenequinide is hydrolysed by *N*/10-hydrochloric acid to *quinide* [quinic acid lactone], m. p. 187° (corr.) after softening at about 172°, $[\alpha]_D^{17}$ −17·13°, in aqueous solution. The isolation of this substance in the optically active form invalidates the arguments of Emde (A., 1918, i, 265), which are based on its supposed inactivity. *Triacetylquinide*, prisms, m. p. 134—135° (corr.), $[\alpha]_D^{15}$ −13·40° in dry acetone, is prepared by the action of acetic anhydride and pyridine on quinide.

[With HEINRICH BAERWIND].—*iso*Propylidenequinide is transformed by methyl iodide and silver oxide in the presence of ether into *methyl*iso*propylidenequinide*, prisms, m. p. 78—79° after softening at 76°, $[\alpha]_D^{23}$ +10·28° in *s*-tetrachloroethane solution.

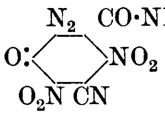
[With HEINRICH OHLENDORF].—Thionyl chloride and pyridine convert *iso*propylidenequinide into the *ester*, $SO(O{\cdot}C_{10}H_{13}O_4)_2$, needles, m. p. 104—105°. H. W.

Purpuric Acids. HANS EDUARD FIERZ and HANS BRÜTSCH (*Helv. Chim. Acta*, 1921, **4**, 375—381).—According to Nietzki and

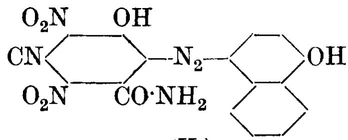
Petri (A., 1900, i, 485), the *iso*purpuric acid obtained from picric acid and potassium cyanide has the annexed structure; the compound formed on diazotisation cannot be coupled with phenols or amines, and is regarded by Nietzki as an *iso*diazoxide. On the basis of the far-reaching analogies between *iso*purpuric acid and ethyl nitrocyanohydroxylaminohydroxybenzoate, the authors conclude that Nietzki's formula is inaccurate and that *iso*purpuric acid is 4 : 6-dinitro-1-hydroxy-2-hydroxylamino-3 : 5-dicyanobenzene (compare Borsche, 1900—1904).



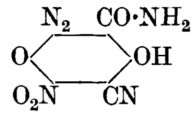
When subjected to diazotisation, this compound undergoes also partial hydrolysis, the resulting product being dinitrocyanocarbamyldiazophenol (I), which reacts with α-naphthol to give the azo-colouring matter (II).



(I.)

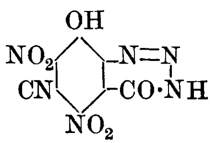


(II.)

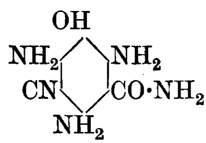


(III.)

The diazotisation product, I, is accompanied by nitrocyanocarbamylhydroxydiazophenol (III). Nietzki's statement that the diazo-compound exhibits abnormal behaviour is explained by the fact that this author repeatedly dissolved the diazo-compound in alkali solution and reprecipitated with acid; the authors find that the dissolution in alkali gives rise almost instantly to the potassium salt of cyanodinitrohydroxybenztriazone (IV), which has the same percentage composition as the diazo-compound itself, is highly explosive, and, on reduction with stannous chloride, is converted into the triaminohydroxycarbamylbenzonitrile (V).



(IV.)



(V.)

Dinitrocyanocarbamyldiazophenol (I) forms lanceolate bundles of narrow, yellow leaflets and explodes at 150—155°. *Nitrocyanocarbamylhydroxydiazophenol* (III) behaves similarly to the preceding compound.

The α-naphthol *azo-colouring matter* (II) crystallises in slender needles with green, metallic lustre and dyes wool bordeaux-red.

After treatment with hydrochloric acid and nitrite, metapurpuric acid shows no sign of coupling and is, therefore, as Borsche assumed (A., 1900, i, 645), a nitroso-compound.

Various examples show that substitution in the $o : o'$-position in the benzene and naphthalene nuclei with amines in general exerts no influence on the orientation of the azo-group in α-naphthol.

T. H. P.

Production of Hydroxyaldehydes and their Derivatives. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIARD, P. MONNET, & CARTIER (Brit. Pat. 161679).—Hydroxyaldehydes

are produced by the action of formaldehyde on a phenol or a phenol derivative, in presence of a nitroso-compound such as nitrosobenzene or nitrosodimethylaniline, and, if necessary, a catalyst. For example, vanillin is obtained by heating for one to two hours a solution of 4 parts of guaiacol, the nitrosodimethylaniline derived from 8 parts of dimethylaniline, and 8 parts of 40% formaldehyde in 50 parts of methyl alcohol, hydrogen chloride being continuously bubbled through. The product is diluted with water, the methyl alcohol distilled off, and the vanillin extracted from the aqueous residue with ether or benzene. The nitrosodimethylaniline is mostly transformed in the process into *p*-aminodimethylaniline. In a similar way, hydroxyaldehydes derived from phenol, anisole, salicylic acid, etc., may be obtained. G. F. M.

γ-Hydroxyaldehydes. III. γ-Hydroxy-γ-phenyl-*n*-butaldehyde. BURCKHARDT HELFERICH and OSKAR LECHER (*Ber.*, 1921, **54**, [*B*], 930—935).—The substance was prepared with the object of examining the effect of the introduction of a phenyl group on the properties of γ-hydroxyaldehydes; it is found that the oxidation of the hydroxyl group is thereby facilitated, since γ-hydroxy-γ-phenyl-*n*-butaldehyde is completely converted into β-benzoylpropionic acid, whereas γ-hydroxyvaleraldehyde can without difficulty be transformed into γ-hydroxyvaleric acid.

ω-Allylacetophenone, b. p. 135—138°/24 mm. (*oxime*, m. p. 53—54°, *semicarbazone*, m. p. 156—157°) is reduced by sodium and boiling ethyl alcohol to *ϵ-hydroxy-ϵ-phenyl-Δ^{α}-pentene*,

$$OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot CH{:}CH_2,$$

a colourless, viscous liquid, b. p. 144—144·5°/28 mm., D_4^{18} 0·980, n_D^{18} 1·5220, the *hydrogen phthalate* of which, m. p. 89—90°, slowly decomposes when preserved. The carbinol is converted by ozone in glacial acetic acid into the corresponding *ozonide*, which is reduced by zinc dust in ethereal solution to formaldehyde and *γ-hydroxy-γ-phenyl*-n-*butaldehyde* (or 5-*hydroxy*-2-*phenyltetrahydrofuran*), $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot CHO$ or $O<\begin{matrix}CHPh-CH_2\\ CH(OH)\cdot CH_2\end{matrix}$, a very viscous liquid, b. p. 137—138°/4 mm., D_4^{18} 1·126, n_D^{18} 1·5410; the substance slowly colours magenta-sulphurous acid solution. Treatment with methyl alcoholic hydrogen chloride (1%) at the ordinary temperature converts it into the methyl *semi-acetal* of γ-hydroxy-γ-phenyl-*n*-butaldehyde [5-*methoxy*-2-*phenyltetrahydrofuran*], a colourless, mobile liquid, b. p. 134—136°/25 mm., D_4^{18} 1·058, n_D^{18} 1·5120.

γ-Keto-γ-phenyl-n-*butaldehyde*, $COPh\cdot CH_2\cdot CH_2\cdot CHO$, has b. p. 131°/2·8 mm., D_4^{18} 1·134, n_D^{18} 1·5412; it reduces Fehling's solution and ammoniacal silver solution much more readily than does the corresponding hydroxy-aldehyde. It is oxidised on exposure to air to β-benzoylpropionic acid (oxime, m. p. 130—131°). It is transformed by phenylhydrazine in 50% acetic acid solution into 1 : 6-*diphenyl*-1 : 4-*dihydropyridazine*, $NPh<\begin{matrix}CPh{:}CH\\ N=CH\end{matrix}>CH_2$, colourless prisms, m. p. 244—245° (decomp.). H. W.

Keto-enolic Desmotropy. XIII. Triphenylvinyl Alcohol and 9-Benzoylfluorene. KURT H. MEYER and HANS GOTTLIEB-BILLROTH (*Ber.*, 1921, **54**, [*B*], 575—578).—9-Benzoylfluorene (Werner and Schöler, A., 1906, i, 436) exists entirely in the ketonic form, since it is insoluble in cold dilute alkali and does not decolorise bromine in freshly-prepared alcoholic solution. It can be converted into the corresponding *enol* by the action of cold dilute sodium hydroxide on its solution in a mixture of chloroform and methyl alcohol, followed by partial removal of the solvent in a current of air and addition of the residue to cold dilute hydrochloric acid or by solution in diethylamine and acidification of the crystalline *diethylamine* salt. When freshly prepared, phenyldiphenylenevinyl alcohol is completely soluble in cold dilute alkali, instantaneously decolorises bromine, but does not give a coloration with ferric chloride; it becomes almost completely converted into the ketonic modification in the course of a few hours. In solution, its enolisation constant is 0·4.

A comparison with the two substances just described indicates strongly that the so-called triphenylvinyl alcohol, $CPh_2\text{:}CPh\cdot OH$, is actually a ketone, $CHPh_2\cdot COPh$. It is insoluble in alkali and does not react with bromine in alcoholic solution. Its tendency towards enolisation is very slight (resembling that of ethyl malonate) since the sodium salt derived from the enolic form immediately gives the ketone when decomposed by water. The term triphenylvinyl alcohol should be deleted from the literature and replaced by triphenylethanone. H. W.

Oxidation of α-Methyl-α-allyl*cyclo*hexanone by Permanganate in Alkaline Solution. R. CORNUBERT (*Compt. rend.*, 1921, **172**, 982—984).—The oxidation of α-methyl-α-allyl*cyclo*-hexanone by potassium permanganate in the presence of soda-lime has proceeded as in the oxidation of dimethylallylacetophenone (compare Haller and Meyeringh, A., 1914, i, 968), the products being a *glycol*, $CH_2{<}{CH_2\cdot CH_2 \atop CH_2{-}CO}{>}CMe\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, m. p. 99·5—100°; b. p. 185—188°/21 mm., giving a *benzoyl* derivative, m. p. 141—142° (corr.), a small amount of a *compound*,

$$O\left[CH_2\cdot CH(OH)\cdot CH_2\cdot CMe{<}{CH_2\cdot CH_2 \atop CO{-}CH_2}{>}CH_2\right]_2,$$

b. p. 260—280°/21 mm., and an *acid*, having the constitution $C_6H_8MeO\cdot CH_2\cdot CH(OH)\cdot CO_2H$ or $C_6H_8OMe\cdot CH_2\cdot CO\cdot CO_2H$. In the presence of potassium hydroxide, the products of oxidation were abnormal, being a very small amount of the *lactone*,

$$C_6H_8MeO\cdot CH_2\cdot CH{<}{CH_2, \atop |\atop O}$$

b. p. 128—131° (corr.) /30 mm., a considerable amount of a resin, b. p. 170—175°/25 mm., probably a trimeride of this ethylene oxide, a small amount of the glycol, and the acid previously mentioned. W. G.

Combined Auxochromes. HUGO KAUFFMANN (*Ber.*, 1921, **54**, [*B*], 795—802. Compare A., 1917, i, 394).—With this title, the

author describes such auxochrome-like groups of atoms as exhibit increased auxochromic character on account of the presence in them of true auxochromes. Their properties are examined in the particular case of the dimethoxystyryl group, the *p*-nitrophenyl residue being used as chromogen. It is shown that the utility of styryl for the formation of combined auxochromes depends on the immediate attachment of its ethylenic linking to the benzene nucleus, since substances such as 2′ : 4′-dimethoxyphenyl 4-nitrostyryl ketone are only feebly coloured. The total 2 : 4-dimethoxystyryl complex is to be regarded as a new auxochromic unit; the ordinary rules of the effect of the position of substituents on the depth of colour do not hold in the cases of the compounds formed from it, since they are developed in cases in which the auxochrome and chromophor are attached to one and the same benzene nucleus. The combined auxochromes, like the usual substances, are in a position to favour fluorescence; thus the *p*-dimethylamino-group does not induce fluorescence of the benzene nucleus of nitrobenzene (dimethyl-*p*-nitroaniline) whereas 4-nitro-4′-dimethylaminostilbene is intensely fluorescent. The power of fluorescing exhibited by the benzene nucleus of nitrobenzene increases when methoxy-groups are introduced into the styryl complex.

The following new substances are described: p-*methoxyphenyl* 4-*nitrostyryl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, from *p*-nitrobenzaldehyde and *p*-methoxyacetophenone in alcoholic solution in the presence of sodium hydroxide, pale greenish-yellow needles, m. p. 169°; 2 : 4-*dimethoxyphenyl* 4-*nitrostyryl ketone*, pale yellow needles, m. p. 191°; 4-*nitro*-2′ : 4′-*dimethoxystilbene*,

$$C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

long, tile-red needles, m. p. 116° (a second, polymorphic *form*, orange-yellow crystals, may be obtained by crystallisation from light petroleum); 4-*nitro*-3′ : 4′-*dimethoxystilbene*, small, yellow crystals, m. p. 133°; 4-*nitro*-2′ : 5′-*dimethoxystilbene*, yellow needles, m. p. 118°. H. W.

***iso*Curcumin. III.** GUSTAV HELLER (*Ber.*, 1921, **54**, [*B*], 1118—1119).—The condensation of vanillin and acetylacetone leads to the production of very small amounts of β-*iso*curcumin, the main product being the non-homogeneous α-*iso*curcumin (A., 1914, i, 563; 1915, i, 417). The application of the process to other aldehydes has shown that the reason for the poverty of yield lies in the decomposition by the alcoholic hydrogen chloride of acetylacetone into acetone, which then preferably condenses with the aldehyde.

[With FRANZ BOBACH].—Acetylacetone and *p*-hydroxybenzaldehyde yield di-*p*-hydroxystyryl ketone, $CO(CH{:}CH{\cdot}C_6H_4{\cdot}OH)_2$. Thymolaldehyde and acetylacetone give *di*-4-*hydroxy*-2-*methyl*-5-iso*propylstyryl ketone*, $CO(CH{:}CH{\cdot}C_6H_2MePr^{\beta}{\cdot}OH)_2$, reddish-yellow crystals, m. p. 268° (decomp.); the corresponding *hydrochloride* forms green needles, the *diacetyl* derivative has m. p. 129°. H. W.

Acetylnaphthols [Hydroxynaphthyl Methyl Ketones]. K. FRIES (*Ber.*, 1921, **54**, [*B*], 709—714).—A substance which is designated 3-hydroxy-β-naphthyl methyl ketone has been obtained by

Witt and Braun (A., 1915, i, 416) by the action of acetyl chloride and aluminium chloride on nerolin. The ability of this substance to form azo-dyes is regarded as evidence of the free α-position, but, since it is not shown that the acetyl group remains intact in them and the latter is known to suffer occasional displacement during this reaction, the evidence is not conclusive. The direct comparison of the product with 2-hydroxy-α-naphthyl methyl ketone, however, has confirmed the structure of Witt and Braun's product.

[With K. FRELLSTEDT].—1-Hydroxy-β-naphthyl methyl ketone is obtained in 50% yield by the action of aluminium chloride on α-naphthyl acetate at 125°, 1-hydroxy-2 : 4-naphthylene dimethyl diketone, m. p. 141° (Webb and Braun, *loc. cit.*, give 140°) being simultaneously produced. It is most readily converted into its methyl *ether*, colourless plates, m. p. 49°, by methyl sulphate and 2*N*-sodium hydroxide at the atmospheric temperature.

2-*Hydroxy-α-naphthyl methyl ketone*, pale yellow needles or rhombic platelets, m. p. 64°, is prepared from β-naphthyl acetate and aluminium chloride. It yields intensely yellow alkali salts. The *methyl* ether crystallises in large, pale yellow prisms, m. p. 59°. With ethyl chloroformate, the naphthol gives the corresponding *ethylcarbonato*-compound, colourless needles, m. p. 60°. Bromine in chloroform solution converts it into 1-bromo-β-naphthol, m. p. 82°; diazobenzene-*p*-sulphonic acid gives β-naphthol orange, the acetyl group suffering replacement during the reaction. Bromine transforms acetylcarbethoxynaphthol into 2-*ethylcarbonato-α-naphthyl bromomethyl ketone*, $CH_2Br{\cdot}CO{\cdot}C_{10}H_6{\cdot}O{\cdot}CO_2Et$, plates, m. p. 79°, which has not up to the present been converted into 4 : 5-benzocumaranone. 2-Hydroxy-α-naphthyl methyl ketone condenses with chloroacetic acid in alkaline solution to form the *compound* $COMe{\cdot}C_{10}H_6{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, colourless leaflets, m. p. 145°, which is converted at 180—210° into a mixture of glycollic acid β-naphthyl ether, m. p. 155° and 3-methyl-4 : 5-benzocumarone, $C_{10}H_6{<}{\scriptstyle\genfrac{}{}{0pt}{}{CMe}{-O-}}{\gg}CH$, m. p. 60°.

H. W.

Researches on Co-ordination and Residual Affinity. IV. The Constitution of Simple and Complex Cobaltic Quinone-oxime Lakes. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1921, **119**, 704—716).

Preparation of 1 : 4-Chloronitroanthraquinones. FRITZ ULLMANN (D. R.-P. 332853; from *Chem. Zentr.*, 1921, ii, 805).—2 : 4-*Dinitro*-1-*hydroxyanthraquinone* is treated with arylsulphonyl-chlorides in the presence of acid fixing materials. In the presence of potassium hydroxide, a replacement of the hydroxyl group by chlorine takes place with formation of 1-*chloro*-2 : 4-*dinitroanthraquinone*; slender, yellow needles, m. p. 240°. On warming with β-naphthylamine in amyl alcoholic solution, the violet-red 1-β-*naphthylaminoanthraquinone* is obtained. 2 : 4-Dinitro-1-hydroxy-

anthraquinone when heated with *p*-toluenesulphonyl chloride and diethylaniline gives 1 : 2-*dichloro*-4-*nitroanthraquinone*; yellow needles, m. p. 246°. By boiling with *p*-toluidine and sodium acetate, blue 2-*chloro*-1 : 4-*ditoluidinoanthraquinone* is obtained. By de-amidising the 1 : 2-dichloro-4-aminoanthraquinone (obtained by reduction), 1 : 2-dichloroanthraquinone is formed. 2 : 4-*Dinitro*-1-*hydroxyanthraquinone*, obtained by nitration of 1-hydroxyanthraquinone, gives slender yellow needles, m. p. 248°. G. W. R.

Preparation of Borneol. FABRIQUES DE PRODUITS CHIMIQUES DE THANN ET DE MULHOUSE (Brit. Pat. 144604).—Turpentine or crude pinene is heated with a quarter of its weight of tetrachlorophthalic acid in a reflux apparatus with continual stirring for twelve hours at 106—108°. The temperature is then slowly raised to 140°, at which it is maintained for six hours. After cooling, the unattacked terpenes are distilled off with steam or in a vacuum, and the residue, which consists of a glassy mass of dibornyl tetrachlorophthalate, is hydrolysed with alcoholic sodium hydroxide. The borneol, precipitated by the addition of water after the removal of the alcohol, is purified by the usual methods. It is optically active and, unlike the product obtained by the action of other organic acids on pinene, it is quite free from *iso*borneol. The yield may be as high as 18% of the crude pinene used, and in addition there is a considerable quantity of pinene recovered, which, if desired, can be returned to the manufacture. The tetrachlorophthalic acid can be almost quantitatively recovered. G. F. M.

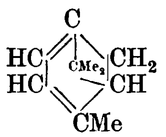
Condensation Products of Phenylhydroxylamine with Hydroxymethylene-compounds and Carbinols. I. Hydroxymethylenecamphor and Phenylhydroxylamine. H. RUPE and W. DIEHL (*Helv. Chim. Acta*, 1921, 4, 388—395).—The previous work is continued (A., 1920, i, 237, 239). *Methylenecamphorphenylhydroxylamine*, $C_8H_{14}<\begin{matrix}C{:}CH\cdot NPh\cdot OH\\ |\\ CO\end{matrix}$, obtained by the interaction of hydroxymethylenecamphor and phenylhydroxylamine, either alone at 100° or in presence of acetic acid, forms slender, yellow needles, m. p. 106—107°. The following derivatives were prepared: *Sodium* salt, deep yellow powder. *Copper* salt, $Cu(O\cdot NPh\cdot CH{:}C_{10}H_{14}O)_2$, brownish-black, amorphous powder; when this salt is heated with alcohol, it decomposes, with separation of cuprous oxide and formation of a white oxidation product of methylenecamphorphenylhydroxylamine which decomposes at 205—206°; it may be obtained in various other ways, and is to be described later. The *methyl* ether, $C_{18}H_{23}O_2N$, forms thin, white leaflets, m. p. 75—76°, and is rapidly decomposed in sunlight, with formation of camphorquinone (?). The *acetyl* compound, $C_{19}H_{23}O_3N$, crystallises in thin, white leaflets, m. p. 162—164°. The p-*nitrobenzoyl* derivative, $C_{24}H_{24}O_4N_2$, forms slender, pale yellow needles, m. p. 179·5—180°, and is accompanied by a small proportion of an almost white, possibly isomeric, compound, m. p. 189—190°.

Methylenecamphorphenylhydroxylamine exhibits, therefore, the properties of a moderately strong acid and thus resembles the benzoyl and carbanil derivatives of phenylhydroxylamine (Beckmann and Schönermark, A., 1898, i, 22). The deep orange compound obtained by Wieland and Gambarjan (A., 1906, i, 830) from phenylhydroxylamine and 1-bromo-2 : 4-dinitrobenzene changes readily, even on crystallisation from alcohol, into a less intensely coloured compound, which is insoluble in alkali. By the action of magnesium phenyl bromide on the *N*-phenyl ether of benzaldoxime, Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) obtained a compound insoluble in alkali which they regard as the hydroxylamine derivative, $CHPh_2{\cdot}NPh{\cdot}OH$; this compound has now been obtained by Wittwer by the condensation of diphenylbromomethane with phenylhydroxylamine, the constitution being thus confirmed. Wieland and Gambarjan assume that the acid character of their dinitrophenylhydroxylamine depends on salt-formation by a quinonoid form. With methylenecamphorphenylhydroxylamine there is no question of such a rearrangement, and the acid nature is to be attributed to the union of the phenylhydroxylamine with the doubly unsaturated conjugation of the methylenecamphor.

Reduction of methylenecamphorphenylhydroxylamine by means of zinc dust and acetic acid yields anilinomethylenecamphor, m. p. 165—167° (Bishop, Claisen, and Sinclair, A., 1895, i, 62). When heated with sodium hydroxide solution, methylenecamphorphenylhydroxylamine is resolved into hydroxymethylenecamphor and phenylhydroxylamine, the latter then reducing any of the unresolved compound to anilinomethylenecamphor and being itself converted into nitrosobenzene, which unites with the phenylhydroxylamine to give azoxybenzene.

When treated with thionyl chloride, methylenecamphorphenylhydroxylamine readily yields a compound containing a chlorine atom in place of the hydroxyl group. T. H. P.

Verbenene [Dehydro-α-pinene] and certain of its Derivatives. A. Blumann and O. Zeitschel (Ber., 1921, **54**, [*B*], 887—894. Compare A., 1913, i, 495).—The crude *l*-verbenene obtained from verbenol as described in the previous communication readily combines with bromine in chloroform solution, forming the beautifully crystalline *dibromide*, prisms, m. p. 70—72°, $[\alpha]_D^{15}$ +297·65°, in benzene solution. Similarly, the *dibromide* from *d*-verbenene has m. p. 70—72°, $[\alpha]_D^{18}$ −298·50°, whilst the racemic *compound* crystallises in needles, m. p. 50—52°. The active dibromide is readily transformed by cold, dilute potassium hydroxide solution into the corresponding unsaturated *glycol*, prisms, m. p. 141°, and, apparently, an *oxide*, D^{15} 0·997, $[\alpha]_D$ about −100°, in alcoholic solution. The pure hydrocarbons are regenerated from the dibromides by the action of zinc dust and acetic acid, the products thus obtained having the following physical constants: *l*-verbenene, D^{15} 0·8866, $[\alpha]_D$ −100·61°; *d*-verbenene, D^{15} 0·8867, $[\alpha]_D$ +100·71°, n_D^{20} 1·49800. Oxidation with permanganate converts verbenene into norpinic acid, m. p. 175·5—176·5°,



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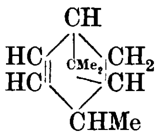


(II.)

whilst treatment with zinc chloride transforms it into *p*-cymene. The mode of preparation and properties of the substance are in harmony with the formula I.

l-Verbenene is reduced by sodium and ethyl alcohol to *dihydroverbenene* [δ-pinene], (II), b. p. 158—159°/762 mm., D^{15} 0·865, D^{20} 0·8625, n_D^{20} 1·4662, $[\alpha]_D$ +36·52°. In its chemical and physical behaviour, this substance very closely resembles α-pinene. It is transformed by hydrogen chloride into pinene hydrochloride, by dilute sulphuric acid into *cis*-terpin hydrate, and by the successive action of nitrosyl chloride and sodium ethoxide into nitrosopinene. Oxidation with permanganate yielded a mixture of acids. H. W.

The Composition of French Oil of Turpentine. M. Vèzes (*Compt. rend.*, 1921, **172**, 977—980).—The polarimetric method described by Darmois (A., 1908, ii, 747; 1910, i, 52; 1911, ii, 352) has been applied to the study of a number of examples of French turpentine, and the results indicate that this method only gives a first approximation of the relative amounts of pinene and nopinene present. Further work is necessary to elucidate the discrepancies found. W. G.

Liquid Crystals of Resin Soaps. Ludwig Paul (*Seifenfabrikant*, 1920, **40**, 425—428, 455—458, 469—472, 503—507, 521, 550—551, 584—585; from *Chem. Zentr.*, 1921, i, 772—773).—A continuation of earlier work on the colloidal characters of colophony. (See *Chem. Zentr.*, 1919, [iv], 667.) A distinction is drawn between the true constituents of colophony, γ- and α-abietic acids, and derivatives of these which differ from them in their colloidal constitution. The occurrence of liquid crystals in the sodium resin soaps is referable to colloidal changes. The resin substances occupy an intermediate position between inorganic colloids and bio-colloids. The colloidal modifications of the true constituents of resin are analogous to inorganic dispersions, which are colloidal modifications of non-colloidal substances. It is suggested that the bio-colloids are colloidal modifications of basal substances, from which they are distinguished by possessing the properties of living matter. G. W. R.

Supersaturated Solid Solutions in Mixtures of Wax–Colophony. Gerhard Jahn (*Koll. Chem. Beihefte*, 1921, **13**, 213—232).—The saturation temperature of bees' wax and colophony mixtures has been investigated, and the optical properties of the solidified mixtures have also been studied. Such mixtures, depending on concentration and temperature, can be divided into (*a*) liquid mixtures, (*b*) solid solutions, (*c*) mixtures in which solid solutions are in equilibrium with pure wax. Mixtures up to 25% of wax can form solid solutions; these possess saturation temperatures at which they are saturated with wax, and on rapidly cooling

to temperatures far below the saturation temperature they form supersaturated solid solutions which may be preserved for long periods. The time for which the supersaturated solution may be kept increases with the length of time the mixture is kept liquid and with the thickness of the preparation; it decreases with the concentration of the mixture. The separation of wax from the supersaturated solutions depends on the power of the wax molecules to diffuse through solid colophony. During the separation of the wax, the ductility of the mixture decreases. The power of turbid media of diminishing the intensity of light increases with the size of the particles which produce the turbidity. J. F. S.

Caoutchouc. Two Dimethylcaoutchoucs. HANS POHLE (*Kolloid Chem. Beihefte*, 1920, **13**, 2—60).—Caoutchouc and two dimethylcaoutchoucs have been investigated in respect of their dispersion and swelling properties in various solvents. Vapour pressure measurements have been made and the relationship of the various forms of caoutchouc to one another considered. It is shown that a coagulation structure does not permanently influence the properties of caoutchouc. Albumins take no part in the solubility relationships, as they do in the case of the resins. In the case of dimethylcaoutchoucs which contain the liquid dispersion medium instead of resins, it is shown that the elasticity is changed in the sense that the temperature limit is lowered, their stability in the air is improved, and vulcanisation is interfered with, but this is only due to the low boiling point of the dispersion medium and can be prevented by the addition of indifferent powders. It is to be regarded as due to the " de-swelling " of certain β-forms of caoutchouc. Three ideal forms, the α-, β-, and γ-modifications, are recognised and characterised by the terms, " non-soluble-swelling," " soluble-swelling," and " soluble-non-swelling," respectively. The three conditions are found in all three caoutchoucs examined, although it is exceptional to find them mixed. In this connection, the caoutchoucs are individually different. An ideal caoutchouc, such as raw rubber, is a system composed entirely of the α- and β-forms. A number of irregular properties of synthetic caoutchouc are to be explained by the constant presence of some of the γ-form. A consideration of the differences of the elastic and other properties of the various modifications allows of their power of taking up the dispersion medium being represented numerically from measurements of the amount of benzene taken up from benzene vapour at constant pressure. These measurements show that, in comparison with the other forms, the γ-form is extraordinarily hygroscopic, and consequently the character of synthetic caoutchouc may be deduced from its hygroscopic properties. The α- and β-modifications have the same hygroscopic properties. Most of the properties of caoutchouc may be deduced from a knowledge of the hygroscopic properties. J. F. S.

Amyrin and Lupeol in the Caoutchouc from *Ficus Vogelii*. A. J. ULTÉE (*Ber.*, 1921, **54**, [*B*], 784—785).—Spence (A., 1907, i, 434) has described the isolation of α- and β-albans, m. p. 201—

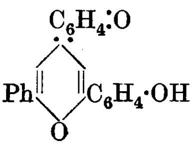
205° and 154° respectively, from *Ficus Vogelii*. The former is shown to be identical with α-amyrin acetate, m. p. 218°; the latter could not be isolated, but a product obtained under the prescribed conditions had m. p. 160—170° which was but little influenced by repeated crystallisation from alcohol and was found to contain lupeol, probably as the acetate. The terms α- and β-alban should be deleted from the literature. H. W.

Mechanism of the Method of Skraup and Priglinger for the Synthesis of Dimethylpyrone. ERNST PHILIPPI and REINHARD SEKA (*Ber.*, 1921, **54**, [*B*], 1089—1091).—Dimethylpyrone has been obtained in about 2% yield by the action of concentrated sulphuric acid on acetic anhydride (Skraup and Priglinger, A., 1910, i, 578), and the following scheme has been provisionally suggested for the reaction:

$$O{<}{\begin{matrix}COMe\\COMe\end{matrix}} + {\begin{matrix}H_2CH\cdot CO\\H_2CH\cdot CO\end{matrix}}{>}O = O{<}{\begin{matrix}CMe{:}CH\\CMe{:}CH\end{matrix}}{>}CO + 2H_2O + CO_2.$$

This hypothesis is supported by the present observations that a better yield of dimethylpyrone (4%) is obtained when sulphuric acid acts on a mixture of acetic anhydride and acetone. If the latter is replaced by methyl ethyl ketone, 2 : 3 : 6-*trimethylpyrone*, m. p. 78°, is produced. This is further identified by transformation into 2 : 3 : 6-*trimethylpyrid*-4-*one*, m. p. 185—192°, by aqueous ammonia at 100°; the corresponding *platinichloride* crystallises in orange-coloured, rectangular plates, m. p. 205°. H. W.

Pyrylium Compounds. X. Violones. W. DILTHEY and B. BURGER (*Ber.*, 1921, **54**, [*B*], 825—830. Compare this vol., i, 190).—It has been shown that pyrylium salts with *p*-hydroxylated phenyl radicles are immediately converted by weak alkalis into coloured anhydro-bases (violones) instead of ψ-bases (A., 1919, i, 413; 1920, i, 323). A further example of this class of compound is now afforded by the isolation of 2-(4)-oxy-4-violone, the constitution of which has not been quite definitely elucidated, but for which the annexed formula is preferred.



A solution of phenyl *p*-methoxystyryl ketone and *p*-methoxyacetophenone in acetic anhydride is converted by hydrated ferric chloride into the *iron* salt, $C_{25}H_{21}OCl_4Fe$, orange-red crystals, m. p. 225°, which is transformed by sodium carbonate into *α-hydroxy-δ-benzoyl-αγ-di-*p*-anisyl-*$\Delta^{\alpha\gamma}$-*butadiene*, $OMe\cdot C_6H_4\cdot C(OH){:}CH\cdot C(C_6H_4\cdot OMe){:}CHBz$, almost colourless crystals, m. p. 97—99°; these rapidly become yellow even in absence of air. The *picrate*, orange-red crystals, m. p. 250—251°, *acid hydrochloride*, $C_{25}H_{21}O_3Cl,HCl$, orange crystals, m. p. 106—107° and 194° (decomp.), after resolidification when rapidly heated (which readily loses 0·5 mol. HCl), and *platinichloride*, orange, crystalline powder, m. p. 235—236°, are described. The ψ-base is converted by concentrated hydrochloric acid at 160—180° into 6-*phenyl*-2 : 4-*di*-p-*hydroxyphenylpyrylium chloride*, dark red crystals or paler prisms, which does not melt below 330°, from which

2-(or 4)-oxy-4-*violone*, $C_5OH_2Ph(:C_6H_4:O)\cdot C_6H_4\cdot OH$, coarse, green crystals, m. p. 317°, is obtained by treatment with hot sodium carbonate solution and subsequent acidification with acetic acid. The corresponding carbinol could not be caused to crystallise, but its *dibenzoyl*-derivative was prepared in colourless prisms, m. p. 147° (picrate, reddish-yellow prisms, m. p. 215°). H. W.

Chromones and Flavones. S. RUHEMANN (*Ber.*, 1921, **54**, [*B*], 912—924).—The methods adopted previously for the synthesis of chromones and flavones have been applied to the preparation of their chloro-derivatives; a smooth reaction is observed with the latter, but not with the former since sulphuric acid of concentration necessary for condensation causes considerable decomposition of the intermediate products.

The preparation of the aryl ethers of β-hydroxycinnamic and hydroxyfumaric esters is effected by the method described previously (T., 1900, **77**, 984, 1119); when, however, the quantity of phenol available is limited, the condensation can be effected by heating the phenylpropiolic or chlorofumaric ester with the sodium phenoxide in boiling xylene.

Ethyl β-5-*methoxy*-m-*tolyloxycinnamate*,

$$OMe\cdot C_6H_3Me\cdot O\cdot CPh:CH\cdot CO_2Et,$$

a yellow, very viscous oil is prepared from the sodium derivative of orcinol methyl ether and ethyl phenylpropiolate, and is hydrolysed to the corresponding *acid*, colourless prisms, m. p. 140° (decomp.), after softening at 122°. The latter is converted by the successive action of phosphorus pentachloride and aluminium chloride into 7(5)-*methoxy*-5(7)-*methylflavone*, colourless needles, m. p. 99—100°, b. p. about 255°/14 mm., which appears to be uniform.

Ethyl o-*chlorophenoxyfumarate*, from sodium *o*-chlorophenoxide and ethyl chlorofumarate, is a colourless liquid, b. p. 203—204°/14 mm. The corresponding *acid*, yellow octahedra, m. p. 202—203° (decomp.), is converted by concentrated sulphuric acid into 8-*chloro-chromone*-2-*carboxylic acid*, $C_6H_3Cl{<}\begin{matrix}CO-CH\\ \quad\;\;\Vert\\ O---C\cdot CO_2H\end{matrix}$, colourless needles, m. p. about 260° (decomp.), which loses carbon dioxide when heated and is thereby transformed into 8-*chlorochromone*, colourless crystals, m. p. 114—115°. Similarly, *ethyl* p-*chlorophenoxyfumarate*, an almost colourless liquid, b. p. 199—200°/12 mm., is transformed successively into p-*chlorophenoxyfumaric acid*, yellow, rhombic crystals, m. p. 211—212° (decomp.), 6-*chlorochromone*-2-*carboxylic acid*, colourless needles, m. p. 261—262° (decomp.), and 6-*chloro-chromone*, colourless, shining needles, m. p. 139—140°.

Sodium *o*-chlorophenoxide and ethyl phenylpropiolate give *ethyl* β-o-*chlorophenoxycinnamate*, $C_6H_4Cl\cdot O\cdot CPh:CH\cdot CO_2Et$, colourless, viscous liquid, b. p. 218—220°/15 mm., which is smoothly converted into β-o-*chlorophenoxycinnamic acid*, colourless prisms, m. p. 160° (decomp.), after softening above 130°. The latter is converted by distillation in a vacuum into α-o-*chlorophenoxystyrene*, $C_6H_4Cl\cdot O\cdot CPh:CH_2$, yellow liquid, b. p. 178°/14 mm., and by successive treatment with phosphorus pentachloride and aluminium

chloride into 8-*chloroflavone*, $C_6H_3Cl<\begin{matrix}CO\text{--}CH\\ \|\\ O\text{---}CPh\end{matrix}$, colourless needles, m. p. 169—170°. Similarly, *ethyl* β-p-*chlorophenoxycinnamate*, coarse, colourless prisms, m. p. 63—64°, b. p. 220—225°/12 mm., is successively converted into β-p-*chlorophenoxycinnamic acid*, colourless prisms, m. p. 136° (decomp.), after softening at 128°, and 6-*chloroflavone*, long, colourless needles, m. p. 183—184°.

Ethyl β-6-*chloro*-m-*tolyloxycinnamate*, from ethyl phenylpropiolate and sodium 6-chloro-*m*-tolyloxide, forms colourless prisms, m. p. 92—93°, b. p. 231—232°/14 mm., and yields the corresponding *acid*, colourless, dendritic prisms, m. p. 155° (decomp.), after softening at about 140°, which is transformed by phosphorus pentachloride and aluminium chloride into a mixture of 6-*chloro*-5-*methylflavone* and 6-*chloro*-7-*methylflavone*, colourless prisms, m. p. 145—147°.

Ethyl β-p-*benzeneazophenoxycinnamate*,

$$N_2Ph\cdot C_6H_4\cdot O\cdot CPh{:}CH\cdot CO_2Et,$$

orange prisms, m. p. 156°, is smoothly hydrolysed to β-p-*benzeneazophenoxycinnamic acid*, yellowish-red prisms, m. p. 184—185° (decomp.), which gives a yellow, *sodium* salt sparingly soluble in water. The acid is converted in the usual manner into 6-*benzeneazoflavone*, yellow prisms, m. p. 194—195°. H. W.

Benzocoumaranones [Naphthafuranones]. K. Fries and R. Frellstedt (*Ber.*, 1921, **54**, [*B*], 715—725).—The experiments were undertaken in the hope of discovering oxindigoid compounds of the naphthalene series which would be less readily hydrolysed than the parent substance (2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran, Fries, Hasselbach, and Schröder, A., 1914, i, 985), and thus would remain undecomposed in the vat.

β-*Naphthyl chloroacetate*, colourless needles, m. p. 96°, is readily obtained by heating β-naphthol with chloroacetyl chloride, and is converted by aluminium chloride into 4 : 5-*benzocoumaran*-3-*one*, $C_{10}H_6<\begin{matrix}CO\\ O\end{matrix}>CH_2$, colourless needles, m. p. 133°, the yield, however, being poor. The corresponding p-*nitrobenzylidene* derivative crystallises in yellow needles, m. p. 270°. With *p*-nitrosodimethylaniline the coumaranone gives the *anil*, $C_{10}H_6<\begin{matrix}CO\\ O\end{matrix}>C{:}N\cdot C_6H_4\cdot NMe_2$, small, red needles, m. p. 231° which, however, could not be caused to interact further with the coumaranone. It is converted by cold concentrated sulphuric acid into 4 : 5-*benzocoumaran*-2 : 3-*dione*, orange-yellow needles, m. p. 182° (decomp.), which reacts readily with *o*-phenylenediamine.

4-*Bromo*-1-*hydroxy*-β-*naphthyl bromomethyl ketone*, yellow needles or prisms, m. p. 147°, is prepared by the addition of bromine to 1-hydroxy-β-naphthyl methyl ketone in chloroform solution, and is converted by treatment with boiling dimethylaniline into 5-*bromo*-6 : 7-*benzocoumaran*-3-*one*, yellow needles, m. p. 158° [p-*nitrobenzylidene* derivative, yellow needles, m. p. 335°; *terephthalylidene* compound, $C_{32}H_{16}O_4Br_2$, yellow needles, m. p. 311° (decomp.)].

5-*Bromo*-2-p-*dimethylaminoanil*-6 : 7-*benzocoumaran*-3-*one*,

$$C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C:N\cdot C_6H_4\cdot NMe_2,$$

crystallises in coarse, dark red needles, m. p. 251° and, under conditions which are not yet quite precisely defined, unites with the parent coumaranone to yield 5 : 5′-*dibromo*-6 : 7 : 6 : 7′-*dibenzo-oxindigotin*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C:C<\underset{-O-}{\overset{CO}{}}>C_{10}H_5Br$, small orange-coloured leaflets, which do not melt below 350°. The action of sodium nitrite on the coumaranone dissolved in glacial acetic acid leads to the formation of 4-*bromo*-1-*oximino-dihydro*-αβ-*naphthafuran*-2-*one*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C:N\cdot OH$, yellow needles, m. p. 207° (decomp.), which is transformed by a boiling mixture of glacial acetic and fuming hydrochloric acids into 4-*bromo*-1-*hydroxy*-β-*naphthylglyoxylic acid*, $HO\cdot C_{10}H_5Br\cdot CO\cdot CO_2H$, yellow needles, m. p. 168° (decomp.); this is also obtained by the action of concentrated sulphuric acid on the anil. The acid reacts with bromobenzo-coumaranone in glacial acetic acid solution in the presence of concentrated sulphuric acid to yield 4 : 4′-*dibromo*-1 : 2′-*bis*[*dihydro*-αβ-*naphthafuran*]-2 : 1-*dione*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C:C\overset{CO-O}{\diagup\!\!-\!\!-\!\!\diagdown}C_{10}H_5Br$, brownish-red needles, m. p. 348—350°, which decomposes in the vat. Isatin and bromobenzocoumaranone give 4-*bromo*-1(3′)-*indoxyl-dihydro*-αβ-*naphthafuran*-2-*one*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C:C<\underset{C_6H_4}{\overset{CO-}{}}>NH$, slender, red needles, m. p. 300° (decomp.), after softening at 290°, which is not recovered unchanged from the hyposulphite vat.

Hydrogen sulphide reacts with a warm solution of the anil in benzene to give 4-*bromo*-1-*thiol*-1-p-*dimethylaminoanilinodihydro*-αβ-*naphthafuran*-2-*one*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C(SH)\cdot NH\cdot C_6H_4\cdot NMe_2$, red needles, m. p. 176° (decomp.), which is transformed by potassium ferricyanide in alkaline, aqueous alcoholic solution into the *spiran*, $C_{10}H_5Br<\underset{-O-}{\overset{CO}{}}>C<\underset{-S-}{\overset{NH}{}}>C_6H_3\cdot NMe_2$, red needles, m. p. 260° (decomp.). H. W.

Oxalyl Chloride. VI. Friedel and Crafts' Reaction with Oxalyl Chloride. H. STAUDINGER, E. SCHLENKER, and H. GOLDSTEIN (*Helv. Chim. Acta*, 1921, **4**, 334—342. Compare A., 1913, i, 604).—The use of oxalyl chloride in Friedel and Crafts' reaction usually results in the formation, not of *o*-diketones, but of ketone derivatives, the oxalyl chloride being decomposed by aluminium chloride into carbon monoxide and carbonyl chloride. From anisole, however, anisil is obtainable (Staudinger, Anthes, and Schöller, A., 1912, i, 567), and anthracene and other condensed hydrocarbons yield aceanthrenequinone and similar compounds (Liebermann and collaborators, A., 1911, i, 387, 656; 1912, i, 464); from naphthalene and oxalyl chloride, however, no acenaphthene-quinone derivative has been obtained. With the object of obtaining

such derivatives, the author has investigated the action of oxalyl chloride on naphthyl ethers (compare Giua, A., 1917, i, 204).

α-Naphthyl methyl ether and oxalyl chloride yield 4 : 4′-dimethoxydi-α-naphthyl diketone, m. p. 228—229° (Giua, *loc. cit.*, gave 230—231°). 4 : 4′-*Diethoxydi-α-naphthyl diketone*,

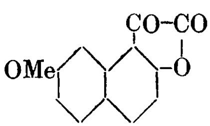
$OEt\cdot C_{10}H_6\cdot CO\cdot CO\cdot C_{10}H_6\cdot OEt$,

forms yellowish-green leaflets, m. p. 220—221°.

β-Naphthyl ethyl ether and oxalyl chloride yield : (1) β-naphthafuran-1 : 2-dione or the lactone of 2-hydroxynaphthoyl-1-formic acid (Giua's lactone of hydroxynaphthylglyoxylic acid), which may also be obtained readily from β-naphthol and oxalyl chloride; (2) a neutral compound which was not investigated, but is probably Giua's ketone, and (3), in small proportion, β-methoxyacenaphthenequinone (compare following abstract). The condensation of oxalyl chloride with β-naphthyl phenyl or benzyl ether yields no definite products. 2 : 7-Dimethoxynaphthalene and oxalyl chloride yield but little 2 : 7-dimethoxyacenaphthenequinone (compare following abstract), the main product being 7-methoxy-β-naphthafurandione (lactone of 2-hydroxy-7-methoxynaphthoylformic acid). The methylation of 1 : 8-dihydroxynaphthalene has as yet yielded, not the dimethyl ether, but only the monomethyl ether, which is unsuitable for condensation with oxalyl chloride.

Oxalyl bromide is more sensitive than the chloride towards aluminium chloride and yields diketones the more readily, but with naphthalene only α- and β-naphthoic acids are obtained and with anthracene only a small proportion of aceanthrenequinone. On the other hand, the phenol ethers appear to react readily with oxalyl bromide, giving rise to *o*-diketone derivatives.

β-Naphthafuran-1 : 2-dione has m. p. 183° (decomp.); Giua (*loc. cit.*) gave m. p. 178° (decomp.), and, like simple coumarandione derivatives, reacts with phenylhydrazine and with *o*-phenylenediamine.



7-*Methoxy-β-naphthafurandione* (*lactone* of 2-*hydroxy-7-methoxynaphthoylformic acid*) (annexed formula), forms brownish-yellow crystals, m. p. 184° (decomp.).

1-*Hydroxy-8-methoxynaphthalene*,

$OH\cdot C_{10}H_8\cdot OMe$,

forms white crystals, m. p. 55—56°, gives a deep red coloration with ferric chloride in alcoholic solution, and undergoes gradual decomposition in the air. T. H. P.

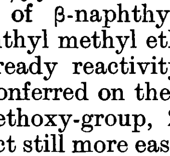
Oxalyl Chloride. VII. Friedel and Crafts' Reaction with Iminochloride Derivatives of Oxalic Acid. H. STAUDINGER, H. GOLDSTEIN, and E. SCHLENKER (*Helv. Chim. Acta*, 1921, **4**, 342—364).—Owing to the decomposition of oxalyl chloride into carbon monoxide and carbonyl chloride by aluminium chloride, the authors have investigated the application to the Friedel and Crafts' reaction of phenyloxalimino-chloride. It is found that phenyliminochlorides react far less energetically than the corresponding acid chlorides. Thus, with phenyloxalimino-chloride, benzene yields no benzil; anisole gives anisil, although the latter is difficult to

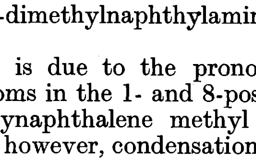
isolate owing to the partial conversion of the iminochloride into a brown, amorphous mass; naphthalene yields acenaphthenequinone in very small amount; α-naphthyl methyl ether gives no definite products, but β-naphthyl methyl and ethyl ethers readily yield β-methoxy- and β-ethoxy-acenaphthenequinones. The latter compounds, like their parent substances, may be used for the synthesis of colouring matters.

The condensation with phenyloxalimino-chloride of β-naphthyl phenyl and benzyl ethers produces acenaphthenequinone derivatives in very small yields, whilst β-naphthyl benzoate and acetate give no such derivatives. From β-naphthol itself no β-hydroxyacenaphthenequinone is obtained, β-naphthafuran-1 : 2-dione being formed in about 75% yield. No condensation occurs with either the benzoyl derivative of β-naphthylamine, or β-dimethylnaphthylamine, or β-thionaphthyl methyl ether.

If the ready reactivity of neroline is due to the pronounced mobility conferred on the hydrogen atoms in the 1- and 8-positions by the methoxy-group, 2 : 7-dihydroxynaphthalene methyl ether should react still more easily; actually, however, condensation to an acenaphthenequinone derivative proceeds even less readily in this case. With 2 : 6-dimethoxynaphthalene also the reaction fails almost entirely. Anthracene gives a very small yield of aceanthrenequinone (compare Liebermann and Zsuffa, A., 1911, i, 387), and β-methylanthracene and β-methoxyanthracene react only very incompletely. Other hydrocarbons, such as diphenyl, fluorene, phenanthrene, and acenaphthene, give no condensation products with iminochlorides.

β-*Methoxyacenaphthenequinone* (I), crystallises in yellow leaflets, m. p. 215—216°, dissolves in concentrated sulphuric acid to a deep red solution, and condenses with *o*-phenylenediamine, giving the

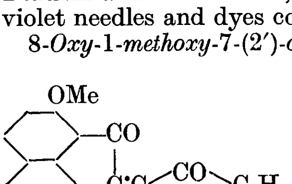
(I.) 

(II.) 

quinoxaline derivative (II), which crystallises in pale yellow needles, m. p. 182—183·5°.

8-*Oxy*-1-*methoxy*-7-(2′)-*indoxylacenaphthene*, $C_{21}H_{13}O_3N$ (compare Bezdzik and Friedländer, A., 1908, i, 673), crystallises in blackish-violet needles and dyes cotton bluish-violet.

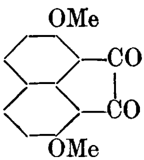
8-*Oxy*-1-*methoxy*-7-(2′)-*oxythionaphthenylacenaphthene* (annexed formula), is a red compound, which colours cotton deep red and dissolves in concentrated sulphuric acid to a deep blue solution.



β-*Ethoxyacenaphthenequinone*, $C_{14}H_{10}O_3$, forms crystals, m. p. 141—142°, and condenses with *o*-phenylenediamine, with indoxyl, and with thioindoxyl.

β-*Methylthiolnaphthalene* has m. p. 59—60°, b. p. about 173°/15 mm.

2 : 7-*Dimethoxyacenaphthenequinone* (annexed formula), forms an orange-red powder, m. p. 273°, gives a deep blue solution in sodium hyposulphite and sodium hydroxide solution, and condenses with indoxyl and with thioindoxyl.



Tolyloxalimino-chloride (compare Bauer, A., 1907, i, 603) condenses with β-methoxynaphthalene to form β-methoxynaphthenequinone, but in smaller yield than is obtained from phenyloxalimino-chloride; with benzene, it condenses to only a small extent.

m-*Nitrophenyloxalimino-chloride*,

$$NO_2{\cdot}C_6H_4{\cdot}N{:}CCl{\cdot}CCl{:}N{\cdot}C_6H_4{\cdot}NO_2,$$

forms pale yellow crystals, m. p. 173°.

α-*Naphthyloxalimino-chloride*, $C_{10}H_7{\cdot}N{:}CCl{\cdot}CCl{:}N{\cdot}C_{10}H_7$, crystallises in slender, golden needles, m. p. 156—156·5°, and dissolves in concentrated sulphuric acid to a deep violet solution, which, when heated, loses hydrogen chloride and becomes indigo-blue and then darkens.

β-*Naphthyloxalimino-chloride*, $C_{22}H_{14}N_2Cl_2$, crystallises in sulphur yellow leaflets, m. p. 210—211° (decomp.). T. H. P.

Dibenzothianthrenediquinone. KURT BRASS and LUDWIG KÖHLER (*Ber.*, 1921, **54**, [*B*], 594—597).—2:3-Dichloro- (or dibromo-) α-naphthaquinone reacts readily with sodium sulphide in alcoholic solution or when the substances are triturated together, with the formation of *dibenzothianthrenediquinone*, $C_{10}H_4O_2{<}{}^{S}_{S}{>}C_{10}H_4O_2$, long, pointed, violet-red needles, m. p. 309°, which is best prepared by heating the materials together until the sulphide has become completely dehydrated, diluting the product with water, agitating with air, and completing the oxidation with hydrogen peroxide. Reduction with zinc dust and acetic anhydride leads to the formation of *tetra-acetoxydibenzothianthrene*, colourless leaflets, whilst the *tetrabenzoyloxy*-derivative is conveniently prepared by the action of benzoyl chloride on the hyposulphite vat of the quinone. The free *quinol* is obtained by the reduction of an alkaline suspension of the 2 : 3-dichloro-α-naphthaquinone with hydrogen sulphide. The sodium sulphide or alkaline hyposulphite vat exhibits little affinity for the unmordanted vegetable fibre. H. W.

Syntheses of Homomorpholine and Benzohomomorpholine. JULIUS VON BRAUN and OTTO BRAUNSDORF (*Ber.*, 1921, **54**, [*B*], 685—703).—Previous investigations (A., 1905, i, 826; 1910, i, 821; 1913, i, 197) have shown that it is possible to introduce an additional methylene group into the piperidine and benzopiperidine rings with the formation of hexamethyleneimine and homotetrahydroquinoline respectively. After a number of unsuccessful attempts, the authors have now succeeded in similarly enlarging the morpholine and benzomorpholine rings.

γ-Bromopropyl benzoate reacts with an excess of ammonia in

benzene solution at 100° to yield a complex mixture of bases from which it was only possible to isolate relatively small amounts of approximately pure *γ-aminopropyl benzoate*, b. p. 150°/15 mm. Under similar conditions, methylamine gives small amounts of *γ-methylaminopropyl benzoate*, a colourless liquid, b. p. 144—145°/10 mm., and very much larger amounts of *di-γ-benzoyloxypropylmethylamine*, $NMe(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OBz)_2$, colourless, very viscous liquid, b. p. 268—272°/6 mm. (the *hydrochloride*, leaflets, m. p. 137°, *auri-* and *platini-chlorides*, and *methiodide*, m. p. 187°, are described). The base is hydrolysed by aqueous-alcoholic sodium hydroxide solution to *methyldi-γ-hydroxypropylamine*, $NMe(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, a colourless oil, b. p. 164—165°/13 mm., which gives a *picrolonate*, m. p. 136°, a *methiodide*, small needles, m. p. 110°, and a non-crystalline *hydrochloride*, *aurichloride*, and *platinichloride*. The poor yields of the compounds just described inhibited their further use for the present purpose.

γ-Anilinopropyl benzoate is readily prepared by the interaction of aniline and γ-bromopropyl benzoate at 100°, but its isolation in the pure condition could not be effected. The crude product is readily hydrolysed to *N*-γ-hydroxypropylaniline, b. p. 173—180°/10 mm., D_4^{19} 1·073 (compare Rindfuss and Harnack, A., 1920, i, 681), which gives a non-crystalline *nitroso*-derivative, *hydrochloride*, and *platinichloride*, a *picrate*, m. p. about 70°, *picrolonate*, m. p. 165°, and *methiodide*, large plates, m. p. 135°. The small residue left on distillation of the base consists of *di-γ-hydroxypropylaniline*, a very viscous, yellow oil, b. p. about 240—245°/10 mm. (*picrate*, m. p. 108°). Hydroxypropylaniline combines with ethylene oxide, yielding N-*γ-hydroxypropyl*-N-*β-hydroxyethylaniline*,

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}NPh{\cdot}[CH_2]_3{\cdot}OH,$$

an almost colourless, viscous liquid, b. p. 220—225°/9 mm., D_4^{17} 1·099 (*picrate*, m. p. 102°; the *hydrochloride* and *methiodide* are non-crystalline), which is transformed by very careful treatment with sulphuric acid (70%) at 160—165° into N-*phenylhomomorpholine*, $NPh{<}^{[CH_2]_3}_{[CH_2]_2}{>}O$, a colourless liquid, b. p. 155—158°/9 mm. (the *hydrochloride*, m. p. 168—169°, *platinichloride*, decomp. 196—197°, *picrate*, m. p. 143°, and *picrolonate*, rhombic leaflets, m. p. 162—163°, are described). The base is completely stable towards acetic anhydride or a mixture of acetic and chromic acids, thus indicating that it is impossible for water to have been eliminated during its formation between a hydroxy-group and a hydrogen atom attached to carbon and making it improbable that a shortening of the trimethylene chain has taken place during ring closure. The base does not suffer ring fission when subjected to Hofmann's reaction. It combines with methyl iodide to give a syrupy *methiodide*; the corresponding *methochloride* is likewise non-crystalline, but can be converted into a *platinichloride*, reddish-yellow powder, m. p. 182—183°. Treatment of the methiodide with boiling potassium hydroxide solution leads essentially to a recovery of the tertiary base. The latter is converted by cautious treatment with nitrous acid into p-*nitrosophenylhomomorpholine hydrochloride*, reddish-yellow

crystals from which the oily green *nitroso*-base is readily isolated. It is transformed by boiling sodium hydrogen sulphite solution into homomorpholine, which is isolated as the *hydrochloride*, m. p. 174—175°. The free *base* is a colourless liquid with a pronounced ammoniacal odour; it is very hygroscopic and has not yet been isolated in the analytically pure state. It is a strong secondary amine, gives an oily *nitroso*-derivative, and exhibits the same behaviour as morpholine to the alkaloidal reagents. It is very stable towards hydrolysing agents. The *benzoyl* derivative is a viscous liquid, but the p-*nitrobenzoyl* compound, $C_{12}H_{14}O_4N_2$, has m. p. 83—84°.

γ-Bromopropyl benzoate reacts readily with a slight excess of *o*-anisidine at 100° to yield γ-*anisidinopropyl benzoate*, which, on hydrolysis, yields γ-*hydroxypropyl*-o-*anisidine*,

$$OMe\cdot C_6H_4\cdot NH\cdot [CH_2]_3\cdot OH,$$

a colourless liquid, b. p. 194—196°/10 mm. (the *hydrochloride* is solid but very hygroscopic, the *picrate* is non-crystalline, but the *picrolonate* has m. p. 160—161°, exhaustive methylation gives the quaternary *iodide*, $OMe\cdot C_6H_4\cdot NMe_2I\cdot [CH_2]_3\cdot OH$, m. p. 163°; the *nitroso*-compound is an oil). Treatment of γ-hydroxypropyl-*o*-anisidine with fuming hydrochloric acid at 160° leads to the production of N-γ-*chloropropyl*-o-*aminophenol hydrochloride*, colourless, crystalline powder, m. p. 168—170°, from which the free *base*, $OH\cdot C_6H_4\cdot NH\cdot [CH_2]_3\cdot Cl$, almost colourless crystals, m. p. 76—77°, is isolated; the latter is extremely unstable towards moisture, and could not therefore be converted into a picrate or platinichloride. It gives a characteristic *nitroso*-derivative, m. p. 96—97°. Ring closure is most readily effected by warming the base with about one molecular proportion of alkali hydroxide, thereby giving *benzohomomorpholine*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{O-CH_2}{NH\cdot CH_2}}{>}CH_2$, in 10% yield; the new base could not be obtained completely free from halogen, but it yields a homogeneous *picrate*, m. p. 190° after darkening at 160°, and *methiodide*, long needles, m. p. 175—176°. The possibility that ring closure is effected in such a manner as to yield the compound $C_6H_4{<}{\genfrac{}{}{0pt}{}{O-CH_2}{NH\cdot CNMe}}$ is excluded, since the picrate of the latter has m. p. 141°. The second possibility of formation of the substance, $C_6H_4{<}{\genfrac{}{}{0pt}{}{O-CHMe}{NH\cdot CH_2}}$, is also excluded, since the quaternary iodide of benzohomomorpholine is converted by Hofmann's reaction into *o*-dimethylaminophenyl allyl ether, $NMe_2\cdot C_6H_4\cdot O\cdot C_3H_5$. The latter substance is prepared in the following manner. *o*-Nitrophenyl allyl ether (Claisen and Eisleb, A., 1913, i, 1175) is reduced by stannous chloride and hydrochloric acid to o-*aminophenyl allyl ether*, a colourless liquid, b. p. 129—130°/10 mm. (*picrate*, m. p. 167—168° after darkening at 162°; *hydrochloride*, m. p. 182—183°; *phenylthiocarbamide*, m. p. 117°). The latter is converted by exhaustive methylation into the quaternary *iodide*, m. p. 181—182° which, when heated in a vacuum, is decomposed into methyl iodide and o-*dimethylaminophenyl allyl ether*, b. p. 118—119°/10 mm.

(*picrate*, needles, m. p. 166—167°; the *hydrochloride* is not crystalline, *platinichloride*, ochre-yellow powder, m. p. 160—161°). H. W.

Ring Closure with Polycarboxylic Acids. II. Course of the Amidation of Ethanetetracarboxylic Ester, Ethanehexacarboxylic Ester, and Methane-tri- and -tetra-carboxylic Esters. ERNST PHILIPPI, JULIE HANUSCH, and ANTON VON WACEK (*Ber.*, 1921, **54**, [*B*], 895—902. Compare Philippi and Hanusch, A., 1920, i, 594).—Ethyl ethanetetracarboxylate is most conveniently converted into the corresponding tetra-amide (long, transparent crystals) by the action of liquid ammonia at the ordinary temperature. The substance rapidly loses a molecular proportion of ammonia when preserved, yielding 2 : 5-*dioxopyrrolidine*-3 : 4-*dicarboxylamide*, $HN<\begin{matrix}CO\cdot CH\cdot CO\cdot NH_2\\ | \\ CO\cdot CH\cdot CO\cdot NH_2\end{matrix}$. A second molecular proportion of ammonia is eliminated if this substance is heated at 200° in a vacuum, thereby giving the *di-imide* of *ethanetetracarboxylic acid*, $HN<\begin{matrix}CO\cdot CH\cdot CO\\ | \\ CO\cdot CH\cdot CO\end{matrix}>NH$.

Ethyl ethanehexacarboxylate is not affected by dry liquid ammonia at the ordinary temperature or by alcoholic ammonia at any temperature up to 150°.

Ethyl methanetricarboxylate and dry ammonia react with formation of malonamide and urethane. The reaction appears to depend on the preliminary fission of the tricarboxylate into malonic and carbonic esters, and is thus analogous to the effect of hydrolysing agents. The same products are obtained from ethyl methanetetracarboxylate; the primary action appears to consist in the formation of the tricarboxylate. H. W.

The Cinchona Alkaloids. XXII. Synthesis of 3-Acetyl-4-methylpyridine and of β-Collidine. PAUL RABE and ERNST JANTZEN (*Ber.*, 1921, **54**, [*B*], 925—929).—In continuation of previous work (A., 1919, i, 34), the synthesis of these substances from homonicotinic acid is described.

Ethyl homonicotinate, colourless, highly refractive, hygroscopic liquid, b. p. 118°/12 mm. [*picrate*, matted golden needles, m. p. 137° (corr.), *platinichloride*, orange needles, m. p. 183° (corr. decomp.)], condenses with ethyl acetate in the presence of sodium ethoxide and benzene with formation of the β-*ketonic ester*,

$$C_5H_3NMe\cdot CO\cdot CH_2\cdot CO_2Et,$$

which is hydrolysed by alcohol and concentrated hydrochloric acid to 3-*acetyl*-4-*methylpyridine*, a colourless, oily liquid, b. p. 105°/12 mm. *picrate*, golden needles, m. p. 147° (corr.); *platinichloride*, pale ochre-coloured, prismatic needles, m. p. 206—207° (corr., decomp.); *aurichloride*, egg-yellow, unstable precipitate. The ketone is converted by hydrazine hydrate into the corresponding *hydrazone*, which was not isolated in the homogeneous condition; it is, however, smoothly converted by being heated with powdered potassium hydroxide into 4-methyl-3-ethylpyridine (β-collidine), a colourless, hygroscopic liquid, b. p. 76°/12 mm. [picrate, yellow needles,

m. p. 149°/ (corr.), *platinichloride*, orange crystals, m. p. 234—235° (corr., decomp.)]. H. W.

Syntheses of certain Carboxylic and Ketocarboxylic Acids of Pyridine. OTTO MUMM and OTTO BÖHME (*Ber.*, 1921, **54**, [*B*], 726—737).—The synthesis of ethyl 2 : 6-dimethyl-3 : 4-cinchomeronate by the interaction of molar quantities of ethyl acetylpyruvate and ethyl β-aminocrotonate has been described by Mumm and Hüneke (A., 1918, i, 183). The present communication deals with the effect of variation in one or other of the components. It is found that the synthesis is capable of considerable extension.

Ethyl propionylpyruvate, b. p. 80—84°/0·6—1 mm., condenses with ethyl β-aminocrotonate to give *ethyl 2-methyl-6-ethylcinchomeronate*, $\begin{matrix} \mathrm{CEt{\cdot}CH{:}C{\cdot}CO_2Et} \\ \| \qquad\quad | \\ \mathrm{N{\cdot}CMe{=}C{\cdot}CO_2Et} \end{matrix}$, a viscous, yellow liquid, b. p. 140—145°/0·4—0·8 mm. (*picrate*, slender, yellow needles, m. p. 90°). The corresponding *acid* has m. p. 258—259°.

Ethyl benzoylpyruvate and ethyl β-aminocrotonate give a mixture of the primary *additive* product, $C_{18}H_{23}O_6N$, short, prismatic needles, m. p. 148°, and *ethyl 6-phenyl-2-methylcinchomeronate*, long, silky needles, m. p. 73° (*picrate*, m. p. about 83°); the former is immediately and quantitatively transformed into the latter at its melting point, more or less rapidly at the atmospheric temperature. 6-*Phenyl-2-methylcinchomeronic acid* forms rhombic platelets, m. p. 217° (decomp.), after previous darkening.

*Ethyl 2-methyl-6-*n*-propylcinchomeronate*, from ethyl butyrylpyruvate and β-aminocrotonic ester, is a yellow liquid, b. p. 174—176°/12 mm. (*picrate*, m. p. 115—116°); the corresponding acid ($+H_2O$) had m. p. 212° (decomp.).

Ethyl β-aminocrotonate and ethyl *iso*butyrylpyruvate give the primary *additive* compound, $C_{15}H_{25}O_6N$, m. p. 87°, which, slowly at the atmospheric but rapidly at higher temperature, passes into *ethyl 2-methyl-6-*iso*propylcinchomeronate*, a pale yellow liquid, b. p. 178°/13 mm. (*picrate*, m. p. 116°). The free *acid* crystallises in quadratic plates ($+2H_2O$) and (anhydrous) has m. p. 210° (decomp.).

The additive *product*, $C_{16}H_{27}O_6N$, from ethyl dimethylpropionylpyruvate and ethyl β-aminocrotonate, crystallises in short, prismatic rods, m. p. 94°, and is transformed at the ordinary temperature into *ethyl 2-methyl-6-*tert.*-butylcinchomeronate*, b. p. 172°/13 mm. (*picrate*, yellow needles, m. p. 127°). The free *acid* ($+2H_2O$) has m. p. 208° (decomp.) after loss of water of crystallisation at 137°.

Reaction could not be induced between ethyl β-aminocrotonate and acetylacetone, oxymethyleneacetone, or ethyl oxalacetate.

Ethyl 3-acetyl-2 : 6-dimethylpyridine-4-carboxylate, b. p. 154—155°/13 mm., m. p. 30—31° (*picrate*, m. p. 160°), is prepared from molecular quantities of acetylacetonamine and ethyl acetylpyruvate. The corresponding *acid* has m. p. 206—207°. Ethyl acetylpyruvate and benzoylacetoneamine react in the presence of alcoholic hydrogen chloride, giving *ethyl 3-benzoyl-2 : 6-dimethylpyridine-4-carboxylate hydrochloride*, m. p. 188—189°. The free *ester* has b. p. 220°/13 mm., m. p. 66°, whilst the acid has m. p. 255—258° (decomp.). H. W.

Comparative Preparation of Derivatives of Isatin, Phthalimide, Succinimide, and *o*-Hydrazinobenzoic Anhydride. GUSTAV HELLER and PAUL JACOBSOHN (*Ber.*, 1921, **54**, [*B*], 1107—1117).—Ethyl isatin-1-carboxylate undergoes a remarkable transformation into ethyl 2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylate when heated with alcohol (A., 1918, i, 309). A similar change is now recorded with 5-bromo- and 5-chloro-isatin, but not with the somewhat similarly constituted phthalimide, succinimide, or *o*-hydrazinobenzoic anhydride.

N-Sodio-5-bromoisatin is converted by ethyl chloroformate in benzene solution into ethyl 5-bromoisatin-1-carboxylate, pale yellow prisms, m. p. 161°, which is transformed in boiling ethyl alcoholic solution into *ethyl 5-bromo-2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylate*, $C_6H_3Br{<}{\substack{CH(OH)\\ NH\text{———}}}{>}C(OH){\cdot}CO_2Et$, pale yellow leaflets, m. p. 89° (corresponding *acid*, m. p. about 117°); the same change occurs slowly in cold benzene solution, but a similar transformation is not thus observed with the unsubstituted ethyl or methyl ester. Under similar conditions, *ethyl 5-chloroisatin-1-carboxylate*, m. p. about 82°, could not be isolated in the homogeneous condition by reason of its partial conversion into *ethyl 5-chloro-2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylate*, pale yellow, quadratic platelets, m. p. 87°.

Potassium phthalimide and ethyl chloroformate give N-*carbethoxyphthalimide*, m. p. 87—89°, which is unaffected by boiling alcohol and not hydrolysed by sulphuric acid (50%) at 40—50°. It is converted by aqueous sodium hydroxide solution or by cautious treatment with hot water into N-*carbethoxyphthalamic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO_2Et$, colourless needles which partly melt at 66° after softening at about 55°. Silver phthalimide, obtained by precipitation of an aqueous solution of phthalimide with silver nitrate, is converted by ethyl chloroformate into *ethylcarbonatophthalimide*, $CO{<}{\substack{\text{——}N\\ C_6H_4}}{>}C{\cdot}O{\cdot}CO_2Et$, slender needles, m. p. 126—127°, which yields phthalimide when treated with boiling alcohol; a specimen of silver phthalimide, prepared from aqueous silver acetate and phthalimide dissolved in alcohol, gave only phthalimide with ethyl chloroformate.

Potassium succinimide and ethyl chloroformate form N-*carbethoxysuccinimide*, m. p. 44°, which is unaffected by alcohol but is transformed by alcohol into N-*carbethoxysuccinamic acid*, m. p. 161°. *Ethylcarbonatosuccinimide*, prepared from silver succinimide, crystallises in colourless plates, m. p. 110—112°.

o-Hydrazinobenzoic acid is converted by benzoyl chloride in pyridine solution into N^{β}-*benzoyl*-o-*hydrazinobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}NHBz$, colourless, prismatic needles, m. p. 255—256°, which is transformed by cautious treatment with acetic anhydride into N^{α}-*acetyl*-N^{β}-*benzoyl*-o-*hydrazinobenzoic anhydride*, $C_6H_4{<}{\substack{CO-\\ NAc}}{>}NBz$, rhombic plates, m. p. 126—127°; more drastic treatment results in the displacement of the benzoyl group

and formation of N^{α}-N^{β}-diacetyl-*o*-hydrazinobenzoic anhydride. N^{α}-N^{β}-*Dibenzoyl*-o-*hydrazinobenzoic anhydride* crystallises in needles, m. p. 106°; energetic treatment of it with acetic anhydride and sodium acetate results in the displacement of both benzoyl by acetyl groups.

1-*Carbethoxy*-o-*hydrazinobenzoic anhydride*, $CO<\genfrac{}{}{0pt}{}{NH-}{C_6H_4}>N\cdot CO_2Et$, prepared from the anhydride and ethyl chloroformate in cold pyridine solution, crystallises in slender needles, m. p. 193°; it is remarkably resistant to hydrolysing agents and is unaffected by boiling alcohol. The corresponding *methyl* ester, needles, m. p. 198°, is obtained similarly; it is converted by boiling acetic anhydride into 1 : 2-diacetyl-*o*-hydrazinobenzoic anhydride. H. W.

Physical and Physiological Properties of some Hydrogenated Quinoline Compounds. AKIRA SHIMOMURA and JULIUS BEREND COHEN (T., 1921, **119**, 740—747).

Derivatives of certain *o*-Nitroketones. S. GABRIEL and WILH. GERHARD (*Ber.*, 1921, **54**, [*B*], 1067—1078).—*o*-Nitroacetophenone, m. p. 28—29°, is converted by an excess of bromine in glacial acetic acid solution into ω-*dibromo*-o-*nitroacetophenone*, rhombic plates and leaflets, m. p. 84—85°. ω-Bromo-*o*-nitroacetophenone, m. p. 55—56°, yields ω-*phthalimido*-o-*nitroacetophenone*, needles, m. p. 204—205°, from which the phthalimido-group could not be removed smoothly; reduction with stannous chloride converts the substance into ω-*phthalimido*-o-*aminoacetophenone*, lemon-yellow rhombs, m. p. 201—202° (*hydrochloride*, m. p. 240—241°), which is hydrolysed by concentrated hydrochloric acid to ω-o-*diaminoacetophenone*, colourless crystals which become red when preserved, m. p. about 123—128° [*hydrochloride*, $C_8H_{10}ON_2,2HCl,2H_2O$, microscopic needles, m. p. 197—198° (decomp.)].

Ethyl *o*-nitrobenzoylacetate crystallises in needles, m. p. 35—36°. The corresponding acid decomposes smoothly when distilled in a vacuum, into carbon dioxide and *o*-nitroacetophenone. Treatment with ferrous sulphate and excess of ammonia converts it into 2 : 4-dihydroxyquinoline, whilst bromine transforms it into o-*nitrobenzoylbromoacetic acid*, crystalline powder, m. p. 94—95° (decomp.). Methylation of the potassio-derivative of *o*-nitrobenzoylacetic ester yields *ethyl* α-o-*nitrobenzoylpropionate*, which was not isolated in the pure condition, but was transformed by hot hydriodic acid into 2 : 4-*dihydroxy*-3-*methylquinoline*; phosphorus pentachloride converts the latter into 2 : 4-dichloro-3-methylquinoline, m. p. 83—84°.

Reduction of ethyl *o*-nitrobenzoylacetoacetate with phosphorus and hydriodic acid leads to the formation of a mixture of 4-hydroxy-2-methylquinoline and 2 : 4-dihydroxyquinoline. When similarly treated, *o*-nitrobenzoylacetone gives a *base*, $C_{10}H_9O_2N$, microscopic rods, m. p. 247—248° (decomp.) (*hydrochloride*, $C_{10}H_9O_2N,HCl,H_2O$, slender needles, *platinichloride*, flattened needles and rhombs, *hydriodide*, $C_{10}H_9O_2N,HI,H_2O$, colourless crystals); the same

substance is more readily prepared by reduction of the nitrodiketone with stannous chloride. Its constitution has not been finally elucidated and the structure $OH{\cdot}C{<}{\begin{matrix}CH-CMe\\C_6H_4{\cdot}N-\end{matrix}}{>}O$, is assigned to it provisionally and it is regarded as 4-hydroxyquinaldine oxide. Its close relationship to 4-hydroxyquinaldine is shown by its conversion into the latter by red phosphorus and hydriodic acid at 200° and by the formation of 4-chloro-2-methylquinoline (picrate, m. p. 175—176°), when it is boiled with phosphorus trichloride. (4-Chloro-2-methylquinoline forms a *monohydrate*, m. p. 42—43°.) The base, $C_{10}H_9O_2N$, gives a slimy *potassium* salt and a crystalline *sodium* compound, $C_{10}H_8O_2NNa,7H_2O$; the latter is converted by methyl sulphate into the quaternary *sulphate*,

$$OMe{\cdot}C{<}{\begin{matrix}CH-CMe\\C_6H_4{\cdot}NMe\end{matrix}}{>}O \quad \overset{O}{—} SO_4H$$

[the corresponding *picrate* crystallises in needles, m. p. 194° (decomp.); the *chloride* is oily, whereas the *nitrate*, $C_{12}H_{14}O_2N{\cdot}NO_3,H_2O$, forms sparingly soluble needles]. 4-Hydroxyquinaldine oxide gives a *picrate*, needles, m. p. 171°, a *benzoyl* derivative, granules and leaflets, m. p. 236—237°, and a *methiodide*, m. p. 130° (corresponding *picrate*, needles, m. p. 204—205°).

The behaviour of the base, $C_{10}H_9O_2N$, towards nitric acid depends on experimental conditions and, in circumstances which are fully described in the original, leads to the production of 3-nitro-4-hydroxy-2-methylquinoline or 3-*nitro*-4-*hydroxy*-2-*methylquinoline oxide*, decomp. about 227°; the latter yields a *sodium* salt which is transformed by methyl sulphate into the corresponding *methyl ether*, $C_{10}H_7O_4N_2Me$, pale yellow needles, m. p. 192°.

The substance, $C_{10}H_8O_4N_2$, is reduced by phosphorus and hydriodic acid to 3-amino-4-hydroxy-2-methylquinoline, m. p. about 248° (decomp.); the *acetyl* derivative volatilises without melting. With stannous chloride and fuming hydrochloric acid, reduction occurs almost exclusively at the nitro-group and leads to the formation of 3-*amino*-4-*hydroxy*-2-*methylquinoline oxide*, lemon-yellow leaflets and needles, m. p. about 258°, after darkening at 240° (*hydriodide*, $C_{10}H_{10}O_2N_2,HI,2H_2O$, yellow needles, *hydrochloride*, $C_{10}H_{10}O_2N_2,HCl,H_2O$, colourless crystals, which become red at 212°). H. W.

Asymmetric Transformation. HERMANN LEUCHS (*Ber.*, 1921, **54**, [*B*], 830—834).—Attempts to resolve hydrocarbostyril-3-carboxylic acid, $C_6H_4{<}{\begin{matrix}CH_2-CH{\cdot}CO_2H\\NH-CO\end{matrix}}$, by means of quinidine in methyl alcoholic solution have led to the complete conversion of the racemic into the dextro-form, the phenomena being very similar to those observed previously in the case of 1-hydrindone-2-benzyl-*o*-carboxylic acid (Leuchs and Wutke, A., 1913, i, 974). The course of the change depends on the sparing solubility of the quinidine salt of the *d*-acid and the existence in solution of an equilibrium between the acid and its optically inactive enolic form,

$C_6H_4<\begin{matrix}CH_2-C\cdot CO_2H \\ NH-C\cdot OH\end{matrix}$; it may be represented by the scheme: *l*-acid salt $\rightleftharpoons$ enolic acid salt $\rightleftharpoons$ *d*-acid salt $\rightarrow$ cryst.

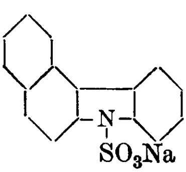
Quinidine d-*hydrocarbostyril-3-carboxylate*,

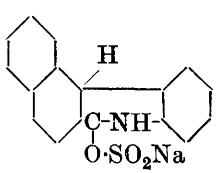
$$C_{20}H_{24}O_2N_2,C_{10}H_9O_3N,2H_2O,$$

has m. p. 138—146° according to the rate of heating, m. p. 138—140° (decomp.) when anhydrous. d-*Hydrocarbostyril-3-carboxylic acid*, $C_{10}H_9O_3N,H_2O$, m. p. 145—146° (decomp.), readily becomes racemised (through the enolic form) when dissolved in glacial acetic acid. By extrapolation, the freshly prepared solution is calculated to have $[\alpha]_D^{18}$ +56·4° for the hydrated acid. H. W.

An Alkylene and some Alkyl Haloids of 2-*p*-Hydroxy-*m*-methoxystyrylquinoline. LOUIS F. WERNER (*J. Amer. Chem. Soc.*, 1921, **43**, 890—891. Compare this vol., i, 54).—2-*p*-Hydroxy-*m*-methoxystyrylquinoline, when heated with an excess of an alkyl or alkylene haloid at 140—155° for four hours in the dark, gave the corresponding derivative, of which the following were prepared: *ethiodide*, m. p. 231° (corr.); *propiodide*, m. p. 221° (corr.); iso*propiodide*, m. p. 266° (corr.); *butiodide*, m. p. 219° (corr.); iso*butiodide*, m. p. 259° (corr.); iso*amyliodide*, m. p. 185° (corr.); *allylobromide*, m. p. 237° (corr.). All these compounds except the *iso*propyl- and the *iso*butyl-iodides act as indicators, giving a fuchsin-red colour with alkali and a pale yellow with neutral or acid acetate. W. G.

The Reaction of Naphthols and Naphthylamines with Bisulphite. P. FRIEDLÄNDER (*Ber.*, 1921, **54**, [*B*], 620—624).—The historical development of the Lepetit-Bucherer reaction is fully described and the views of the course of the change are discussed. Bucherer's supposition that reactive naphthyl sulphites are formed intermediately is scarcely in harmony with the established stability of these compounds; the simplest and most satisfactory explanation lies in the assumption that the phenols react in the tautomeric ketonic form and that the substances formed are normal ketone-sulphite additive products. If this is the case, their molecule must contain one oxygen and two hydrogen atoms more than if they are constituted according to Bucherer's hypothesis, but the available material has been so far unsuitable for deducing analytical evidence on this point. More conclusive evidence is obtained in the following manner. Bucherer and Seyde (A., 1909, i, 735) have obtained a product from β-naphthol, sodium hydrogen sulphite, and phenylhydrazine to which they ascribe the formula (I) and the author assigns the formula (II). The analytical differences between these formulæ are not great, but, according to (I), a reaction between β-naphthol, sodium hydrogen sulphite, and *N*-phenyl-*N*-alkylhydrazine would not be expected to occur, whilst in accordance


(I.)


(II.)

with (II) the ultimate formation of a substance, $\begin{matrix} C_{10}H_6 \\ C_6H_4 \end{matrix}\!>\!N\cdot Alk$, might be expected. It is found that hydroxynaphthoic acid, *as*-methylphenylhydrazine, and sodium hydrogen sulphite react in exactly the same manner as when the simpler phenylhydrazine is used and yield N-*methylnaphthacarbazole*, [7-*Methylbenzo*-β-*naphthindole*], colourless needles, m. p. 121° (*picrate*, red needles, m. p. 171°). The analytical differences between this substance and naphthacarbazole are very slight, but the individuality of the two compounds is shown by the fact that the former is unaffected by potassium hydroxide at 230°, whereas the latter yields a potassium salt which is transformed into methylnaphthaphenocarbazole by gentle treatment with methyl iodide. H. W.

Synthesis of αβ-Diglycerides and Unsymmetrical Triglycerides. MAX BERGMANN, ERWIN BRAND, and FERDINAND DREYER (*Ber.*, 1921, **54**, [*B*], 936—965).—The initial material for the synthesis is 2-phenyl-5-hydroxymethyloxazolidine,

$$OH\cdot CH_2\cdot CH\!<\!\begin{matrix} CH_2\cdot NH \\ O\text{——}CHPh \end{matrix},$$

in which one alcoholic hydroxyl group is already present. A second such group is introduced by the hydrolytic elimination of benzaldehyde, thus giving γ-aminopropylene glycol,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2,$$

whilst a third is introduced by the action of nitrous acid on the base. The presence of nitrogen in the intermediate compounds is of advantage, since it facilitates their purification and analytical control and renders possible the production of optically active fats. The synthesis takes the following course. The initial material is acylated, giving $OAc\cdot CH_2\cdot CH\!<\!\begin{matrix} CH_2\cdot NA \\ O\text{——}CHPh \end{matrix}$, which after removal of benzaldehyde gives diacylaminopropylene glycol,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHA.$$

For the preparation of αβ-diglycerides with the two similar groups, A, this compound is treated successively with phosphorus pentachloride and water which causes migration of A from the nitrogen to the neighbouring oxygen atom, probably through intermediate production of the substance $OA\cdot CH_2\cdot CH\!<\!\begin{matrix} CH_2\cdot N \\ O\text{——}CPh \end{matrix}$, thus yielding $OA\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2,HCl$ which, on deamination, gives $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$. For the preparation of αβ-diglycerides with differing acyl groups, the substance

$$OA\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHA$$

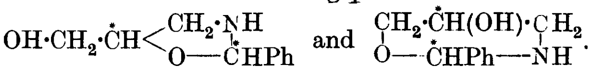
is converted into the compound $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot NHA$ in the usual manner. The latter is treated successively with phosphorus pentachloride and ethyl alcohol whereby an unstable imidoether of the type $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot N{:}CA\cdot OEt,HCl$, is probably formed which is immediately converted by cold dilute hydrochloric acid into $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot NH_2,HCl$ from which the corresponding diglyceride is smoothly produced. A second method of preparing αβ-diglycerides with similar acyl groups is thus also

indicated which follows the lines: $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2 \rightarrow$ $OA\cdot CH_2\cdot CH(OA)\cdot CH_2\cdot NHA \xrightarrow{PCl_5\cdot EtOH,\ etc.}$

$$OA\cdot CH_2\cdot CH(OA)\cdot CH_2\cdot NH_2,HCl.$$

The process is simpler than that first described, but not more advantageous.

The constitution of 2-phenyl-5-hydroxymethyloxazolidine is deduced from the following considerations. The absence of strong basic properties and the production of a dibenzoyl derivative in which one acyl group is attached to nitrogen and the other to oxygen exclude all but the following possibilities:



Since, however, the dibenzoyl derivative after elimination of benzaldehyde can be converted into *s*-dibenzoylnitrobenzoylglycerol, in which both benzoyl groups are present in the α-position, it follows that the dibenzoylaminopropylene glycol must contain its O-benzoyl group in the same position, and consequently also its hydroxyl group previous to acylation. This is only possible with the first formula. It may be noted that two asymmetric centres are present in the compounds which, in accordance with theory, is found to yield two isomeric, optically inactive benzoates; removal of benzaldehyde causes the disappearance of one centre and the isomerides are thereby converted into the same product.

2-*Phenyl-5-hydroxymethyloxazolidine*, prisms, m. p. about 75—79° (probably a mixture of isomerides), is prepared by the action of aminopropylene glycol on benzaldehyde in the presence of ethyl acetate. It is converted by benzoyl chloride in the presence of well-cooled chloroform and pyridine into a mixture of *dibenzoates*, microscopic needles, m. p. 143° (corr.) and m. p. 118° (corr.) respectively, which are separated from one another by a mixture of alcohol and *N*/10-aqueous hydrochloric acid. This is transformed by concentrated hydrochloric acid in the presence of ether into *γ-benzoylaminopropylene benzohydrin*, long, six-sided plates or needles, m. p. 109° (corr.), which is readily converted into N-*γ-benzoylaminopropylene αβ-dibenzoate*, m. p. 113—114° (corr.). When the *ON*-dibenzoate is ultimately mixed with phosphorus pentachloride, warmed for a short time until evolution of hydrogen chloride ceases, and the product is treated with water, the *hydrochloride* of *γ-aminopropylene αβ-dibenzoate*, slender needles, m. p. 203° (corr. decomp.), when fairly rapidly heated, is obtained. The reverse transformation is effected by treatment of an aqueous solution of the hydrochloride (or other salt) with sodium carbonate or sodium acetate. The following *salts* of γ-aminopropylene αβ-dibenzoate, which are generally beautifully crystalline and sparingly soluble in water, are described: *nitrate*, microscopic prisms, m. p. 185° (corr., decomp.); *nitrite*, decomp. 70°; *picrate*, pale yellow, pointed needles, m. p. 187° (corr., decomp.); normal *oxalate*, long needles, m. p. about 173° (corr., decomp.); *hydrogen tartrate*, prismatic needles, decomp. about 184°; *hydrogen saccharate*, slender needles, m. p. about 174° (decomp.). The *benzylidene*

derivative crystallises in long prisms, m. p. about 72—73°. γ-Aminopropylene αβ-dibenzoate hydrochloride is converted by nitrous acid in 50% acetic acid solution at 0° into glycerol αβ-dibenzoate, which could not be caused to crystallise or distilled even in a high vacuum. Its constitution, however, is deduced from its conversion in good yield into glyceryl αβ-dibenzoate α′-*p*-nitrobenzoate, m. p. 114° (corr.), which is found to be identical with the product synthetised previously by Fischer, Bergmann, and Bärwind (A., 1920, i, 805).

Resolution of γ-aminopropylene αβ-dibenzoate is effected by treatment of the aqueous solution of its hydrochloride with silver quinate and crystallisation of the less soluble salt from alcohol. The *quinate* of the *l*-base crystallises in slender, shining needles, m. p. 153° (corr.), $[\alpha]_D^{20}$ −37·79° in aqueous solution, and is converted by concentrated hydrochloric acid into the corresponding *hydrochloride*, needles, m. p. 179° (corr.), $[\alpha]_D^{19}$ −14·25°, in alcoholic (50%) solution. The pure *l*-hydrochloride is transformed into the oily l-*glycerol* αβ-*dibenzoate*, which is converted into l-*glyceryl* αβ-*dibenzoate* α′-p-*nitrobenzoate*, slender needles, m. p. 113·5—114° (corr.), $[\alpha]_D^{20}$ −1·9° in *s*-tetrachloroethane, the first synthesis of a homogeneous, optically active glyceride being thus effected. The small specific rotation appears to be inherent to the substance, and not due to racemisation during its production.

2-Phenyl-5-hydroxymethyloxazolidine is converted by *p*-nitrobenzoyl chloride into a mixture of *di*-p-*nitrobenzoates*, coarse prisms, m. p. 207—208° (corr.), and flat, leafy prisms, m. p. 157—159° (corr.), which, when treated with concentrated hydrochloric acid in the presence of ethyl acetate, yields the ON-*di*-p-*nitrobenzoyl* derivatives of γ-*aminopropylene glycol*, slender needles, m. p. 139° (corr.). The latter is transformed by successive treatment with phosphorus pentachloride and water into the *hydrochloride* of γ-*aminopropylene* αβ-*di*-p-*nitrobenzoate*, four-sided plates, decomp. about 216°; γ-*benzoylaminopropylene* α-*benzoate* β-p-*nitrobenzoate*, oblique prisms, m. p. 154°, is converted by successive treatment with phosphorus pentachloride and ethyl alcohol into γ-*aminopropylene* α-*benzoate* β-p-*nitrobenzoate hydrochloride*, microscopic needles, m. p. 205—206° (decomp.), when fairly rapidly heated (the corresponding *nitrate*, microscopic needles or prisms, and *hydrogen oxalate*, prismatic needles, decomp. 197°, are described); it is converted by the calculated quantity of aqueous sodium hydroxide solution into N-γ-p-*nitrobenzoylaminopropylene benzohydrin*, m. p. 128—129° (corr.). The preparation of γ-aminopropylene αβ-dibenzoate hydrochloride by the action of phosphorus pentachloride and alcohol on the corresponding tribenzoate is also described.

Glycerol α-*benzoate* β-p-*nitrobenzoate*, microscopic needles or thick prisms, m. p. 117—118° (corr.) after softening at 115°, is prepared in the usual manner from γ-aminopropylene α-benzoate β-p-nitrobenzoate hydrochloride and is converted into glyceryl α-benzoate βγ-di-*p*-nitrobenzoate, m. p. 122—123° (decomp.), *glyceryl* αγ′-*dibenzoate* β-p-*nitrobenzoate*, m. p. 86—87°, and *glyceryl* α-*acetate* γ-*benzoate* β-p-*nitrobenzoate*, pale yellow leaflets, m. p. 67—68°.

γ-Aminopropylene α-benzoate β-2 : 4-dichlorobenzoate hydrochloride, m. p. 170–172°, is obtained by the action of 2 : 4-dichlorobenzoyl chloride on the *ON*-dibenzoyl-derivative and subsequent elimination of the *N*-benzoyl group. H. W.

[Constitution of Pyronine, of Salts of Azo-compounds, and of Pyrylium Salts.] F. KEHRMANN (*Ber.*, 1921, **54**, [*B*], 657—659).—A reply to von Braun with regard to the constitution of pyronine (compare von Braun and Aust, A., 1916, i, 663; Kehrmann, A., 1918, i, 449; von Braun, A., 1918, i, 450), to Hantzsch with respect to the constitution of the salts of azo-compounds with acids (Kehrmann and Hempel, A., 1916, i, 165; 1917, i, 593; Hantzsch, A., 1919, ii, 255), and to Dilthey on the constitution of pyrylium salts (A., 1920, i, 324). H. W.

Cyclic Imide Ethers of Diglycollic Acid as Sweetening Agents. MAX SIDO (*Ber. deut. Pharm. Ges.*, 1921, **31**, 118—129).—Whilst the substitution of the imino-hydrogen in "saccharin" by alkyl groups entirely destroys the sweetness of that substance, the position is completely reversed in the case of diglycollimide, which, although itself tasteless, yields alkylimides of the general formula $O<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>NR$, increasing in sweetness with an increasing number of carbon atoms in the alkyl group up to a maximum in the *N*-propyl derivative. The aryl derivatives, on the other hand, are almost tasteless. Diglycollimide was prepared by melting diglycollic acid with ammonium chloride, and crystallising the mass from water after hydrogen chloride had ceased to be evolved. The substituted imides were prepared by melting the alkylamine (or arylamine) hydrogen diglycollates in a vacuum to expel water, and purifying the residual imide by distillation under reduced pressure, followed, if necessary, by crystallisation from alcohol. The diglycollarylimides and also the methyl- and ethylimides are solid, crystalline substances, but the *n*-propyl-, *n*-butyl-, and *iso*butyl-imides form colourless, oily liquids at ordinary temperatures. They are all extremely hygroscopic, and as the absorbed water rapidly reconverts them into the amine hydrogen diglycollates, they are of no practical value as sweetening agents on account of this instability. The following substances are described: *Methylamine hydrogen diglycollate*, $CO_2H\cdot CH_2\cdot O\cdot CH_2\cdot CO_2H,NH_2Me$, prismatic needles, m. p. 140°; *diglycollmethylimide*,

$$O<\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}>NMe,$$

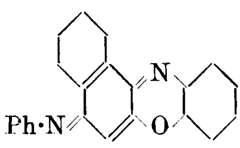
colourless needles with a sweetish taste, m. p. 78°; *ethylamine hydrogen diglycollate*, hygroscopic needles, m. p. 145°; *diglycollethylimide*, very hygroscopic crystals with an extremely sweet but also somewhat phenolic taste; n-*propylamine hydrogen diglycollate*, m. p. 181°; *diglycoll*-n-*propylimide*, a colourless liquid, D_4^{18} 1·1682, of an intensely and purely sweet taste, b. p. 122°/14 mm.; n-*butylamine hydrogen diglycollate*, prisms, m. p. 153°; iso-*butylamine hydrogen diglycollate*, needles, m. p. 142°; *diglycoll*-n-*butylimide*, an oily liquid, b. p. 139°/16 mm., D_4^{18} 1·1346, of intensely sweet taste

and slight anæsthetic properties; *diglycoll*iso*butylimide*, liquid, b. p. 132°/24 mm., D_4^{18} 1·1977, taste bitter; *aniline hydrogen diglycollate*, colourless needles, m. p. 177°; *diglycollphenylimide*, needles, m. p. 195°, o-, m-, and p-*toluidine hydrogen diglycollates* melt at 151°, 138°, and 170° respectively; *diglycoll*-o-*tolylimide*, prisms, m. p. 115·5°; the m-*tolylimide*, leaflets, m. p. 110°, and the p-*tolylimide*, needles, m. p. 182°; *diglycoll*-m-4-*xylylimide*, needles, m. p. 99°, decomposing extremely rapidly in contact with water; and *diglycoll*-p-*ethoxyphenylimide*, colourless needles, m. p. 144°.

G. F. M.

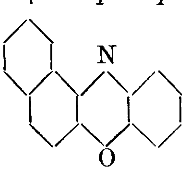
The Synthesis of Oxazines and Thiazines of the Naphthalene Series. I. ZDENKA LUDWIG-SEMELIĆ (*Rev. Chim.*, 1921, **1**, 3—6, 23—25, 40—42).—7 : 12-*Naphthaphenoxazine* (βα-form) has been prepared by condensing 1-amino-β-naphthol with *o*-aminophenol, and has been identified as the by-product which is formed in the preparation of αβ-naphthaphenoxazine from 1 : 2-dihydroxynaphthalene and *o*-aminophenol. Both isomerides possess the property of passing into oxonium salts when subjected to the action of oxidising agents in acid solution, and in this respect they resemble the corresponding thiazines, βα- and αβ-naphthaphenthiazines (obtained by the action of sulphur on the corresponding anilinonaphthalenes), which in similar circumstances yield thionium salts. In all four cases two series of salts are formed, in one of which the organic residue occurs as a univalent ion and in the other as a bivalent ion. The univalent salts are yellow or red, and the bivalent salts blue or violet.

When βα-naphthaphenoxazine is oxidised in alcoholic or acetic acid solution by ferric chloride, 5-βα-naphthaphenoxazone is obtained; similarly, βα-naphthaphenthiazine on oxidation yields the corresponding thiazone. The αβ-derivatives do not exhibit this property. If the oxidation of βα-naphthaphenoxazine is conducted in the presence of an aniline salt the product is the corresponding βα-*naphthaphenoxazine-5-anil* (annexed formula).



At least two nitro-derivatives are formed when βα-naphthaphenothiazine is nitrated. One of these, a *nitrosulphoxide*, may be directly crystallised from the crude nitration product. The other is apparently a *dinitro*-derivative, since on reducing the crude product with stannous chloride and hydrochloric acid and oxidising the precipitated stannochloride by means of ferric chloride there is obtained a *diaminonaphthaphenothiazonium chloride*.

βα-*Naphthaphenoxazine* (annexed formula), prepared by heating at 260° 1-amino-β-naphthol hydrochloride with *o*-aminophenol, forms lustrous yellow plates, m. p. 100° (decomp., 107°) or (decomp.) in a sealed tube filled with carbon dioxide. It can be sublimed. The alcoholic solution shows an intense green fluorescence. The pale blue solution in sulphuric acid is coloured intensely blue by a trace of hydrogen peroxide, the colour being changed to red by addition of ice water.



C. K. I.

Azthionium Salts of the Naphthalene Series. F. KEHRMANN and TAKIS CH. CHRISTOPOULOS (*Ber.*, 1921, **54**, [*B*], 649—657).—A continuation and amplification of previous work (A., 1902, i, 566).

7 : 12-Naphthaphenthiazine, $C_{10}H_6<{NH \atop -S-}>C_6H_4$, golden-yellow platelets, m. p. 130·5°, is conveniently prepared by heating phenyl-α-naphthylamine with sulphur at a temperature not exceeding 210°. It is converted by hydrogen peroxide into the corresponding S-*oxide*, $C_{10}H_6<{NH \atop SO-}>C_6H_4$, colourless, crystalline granules, decomp. 194°. It is oxidised by an excess of ferric chloride to naphthaphenthiazone; the partly oxidised solution deposits dark blue, microscopic needles of the ferric double salt of a quinhydrone-like intermediate compound which is converted by excess of the reagent into the holoquinonoid iron *salt*, $C_{16}H_{10}NSCl,FeCl_3$, dark red needles. The latter is transformed by an excess of perchloric acid (20%) into the *perchlorate*, $C_{16}H_{10}NSClO_4$, dark chocolate-brown needles with a violet glance; the corresponding unstable *perbromide* is also described. This substance is converted by ammonia into 5-imino-7 : 12-naphthaphenthiazine [the base and its hydrochloride have been obtained previously by Stahrfoss (A., 1920, i, 256) in a different manner], the *acetyl* derivative of which crystallises in shining, dark red needles, m. p. 196°.

7 : 12-Naphthaphenthiazine, sulphur-yellow needles, m. p. 178°, is obtained in 80% yield when its components are heated at a temperature not exceeding 210°. The corresponding *acetate* forms colourless crystals, m. p. 126°. The base is converted by sodium nitrite in glacial acetic acid solution into the corresponding S-*oxide*, almost colourless, crystalline granules, decomp. about 225°. It behaves in the same manner as thiodiphenylamine towards ferric chloride since, even with a large excess of the latter, it is only converted into the ferric chloride additive *salt* corresponding with the quinhydrone stage which is transformed by perchloric acid into the *meri*quinonoid *perchlorate*, almost black, microscopic needles. The *holo*quinonoid *perchlorate*, $C_{16}H_{10}NSClO_4$, is most readily prepared by dissolving the sulphoxide in cold concentrated sulphuric acid and adding perchloric acid to the blue solution; the *perbromide*, unstable, dark brownish-red, crystalline powder, is also described.

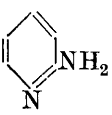
Di-βα-naphthathiazine, $C_{10}H_6<{S- \atop NH}>C_{10}H_6$, pale yellow needles, m. p. 233°, is obtained in 80% yield when β-dinaphthylamine and sulphur are heated for ten minutes at 200—210°. The corresponding *acetate* crystallises in long, colourless needles, m. p. 208·5°, whereas the S-*oxide* forms colourless needles, decomp. 212°. The base is oxidised by an excess of ferric chloride to the *meri*quinonoid double *salt*, graphite-like leaflets. The *holo*quinonoid *perchlorate* is most readily prepared from the sulphoxide.

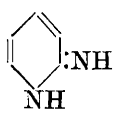
A comparison of the colours of the mono- and di-acid azthionium salts derived from diphenthiazine, αβ-naphthaphenthiazine, and di-αβ-naphthathiazine shows that the positive optical effect of the conversion of the mono- into the di-acid salts is greater when the

molecule in which it occurs is smaller and that the optical result of the gradual enlargement of the molecule of the azthionium compound is negative with the di-acidic but positive with the mono-acidic salts. H. W.

Arylsulphonylnaphthylenediamines and their Sulphonic Acids. GILBERT T. MORGAN and WILLIAM ROBINSON GRIST (T., 1921, **119**, 602—610).

Tautomerism of α-Aminopyridine and its Derivatives. A. E. TSCHITSCHIBABIN, R. A. KONOWALOWA, and A. A. KONOWALOWA (*Ber.*, 1921, **54**, [*B*], 814—822).—In analogy with 2-pyridone, 2-aminopyridine might be expected to yield derivatives of the two forms I and II.


(I.)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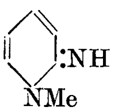
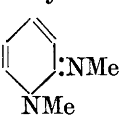
The formation of 2-methylamino- and 2-dimethylamino-pyridine by the action of methyl iodide on the sodium derivative of 2-aminopyridine has been described by Tschitschibabin and Zeide (A., 1915, i, 590); it is now shown that the methyl derivative of the tautomeric form is the main product of the direct action of methyl iodide on the base, and, further, that the possible products are both produced by either method but in relatively greatly differing amounts.

The action of methyl iodide and sodamide on a solution of 2-aminopyridine in dry ether leads to the formation of *2-methylaminopyridine*, colourless, feebly basic liquid, b. p. 200—201° (picrate, m. p. 190°, *loc. cit.*), 2-dimethylaminopyridine and 1-methyl-2-pyridoneimide. 2-Aminopyridine is readily converted by methyl iodide into a *methiodide*, $C_6H_9N_2I$, yellow, prismatic crystals, m. p. 149—150° (*picrate*, lustrous yellow needles, m. p. 201°; *platinichloride*, orange needles, m. p. 204°), which is converted by moist silver oxide into *1-methyl-2-pyridoneimide* (annexed formula),



an almost colourless, crystalline mass, b. p. 108°/16 mm., which darkens and liquefies on exposure to air and readily absorbs carbon dioxide. The picrate, m. p. 201°, is identical with that just described; the *hydrochloride* forms colourless, prismatic crystals, m. p. 110°. The base reacts with phenylcarbimide, yielding a crystalline *substance*, needles, m. p. 148°, and gives a *benzoyl* derivative, golden-yellow crystals, m. p. 70°. The nitroso-derivative has not yet been prepared. The base is slowly converted by boiling aqueous alkali hydroxide solutions into ammonia and 1-methyl-2-pyridone, its constitution being thereby established; its stability towards hydrochloric acid is remarkable. 1-Methyl-2-pyridoneimide reacts vigorously with methyl iodide in alcoholic solution, giving the *methiodide*, $C_7H_{11}N_2I$, colourless prisms, m. p. 159—160° (corresponding *picrate*, m. p. 160°), which is converted by concentrated alkali hydroxide solution into *1-methyl-2-pyridonemethylimide* (annexed formula),



a viscous, yellow liquid, b. p. 128°/38 mm., which darkens on exposure to air and rapidly absorbs carbon dioxide. The base is also formed by the action of methyl iodide on 2-methylaminopyridine.

Benzyl chloride and 2-aminopyridine react in alcoholic solution at the atmospheric temperature to yield 1-*benzyl-2-pyridoneimide hydrochloride*, m. p. 202—203° (*platinichloride*, red, crystalline powder, m. p. 210°), which is not decomposed by sodium carbonate, but from which alkali hydroxide solutions liberate 1-*benzyl-α-pyridoneimide*, very hygroscopic crystals, m. p. 37—39°; the new base is considerably more stable than its methyl analogue, but is slowly transformed by boiling alcoholic alkali hydroxide into 1-*benzyl-α-pyridone*, m. p. 76°. The mother-liquors obtained from the isolation of the hydrochloride, m. p. 202—203°, when treated with sodium carbonate, yielded 2-*benzylaminopyridine*, flattened prisms, m. p. 93—94°, which is fairly stable towards air. The *platinichloride* forms red crystals, m. p. 175°. H. W.

The Action of Methyl Iodide on 2- and 4-Aminoquinolines. A. E. TSCHITSCHIBABIN (*Ber.*, 1921, **54**, [*B*], 822—825).—The reaction has been investigated previously by Claus and Frobenius (A., 1898, i, 150), Claus and Schaller (A., 1898, i, 51), and Roser (A., 1895, i, 155), who have isolated a series of bases by the action of silver oxide or alkali hydroxide on the "methiodides" primarily formed. The unusual properties of these compounds have caused them to be regarded as methylene bases, $CH_2{:}C_9NH_6{\cdot}NH_2$, although their behaviour is only very incompletely explicable by such an assumption. In the light of the similar experience with 2-aminopyridine (preceding abstract), the author shows that the characteristics of the bases soluble in ether are completely in harmony with the conception that they are methylated quinoloneimides, $NH{:}C_9H_6NMe$. H. W.

Di- and Tri-quinolylmethanes united by the Pyridine Nuclei. II. Di-2-quinolylmethane and the Syntheses of ψ-*iso*Cyanine and Quinoline-Red. GÜNTER SCHEIBE [with ERNST ROSSNER] (*Ber.*, 1921, **54**, [*B*], 786—795. Compare this vol., i, 62).—*Di-2-quinolylmethane*, $(C_9H_6N)_2CH_2$, pale yellowish-red, coarse prisms, m. p. 102—103°, after becoming red and softening at 98°, is obtained in admixture with varying amounts of tri-2-quinolylmethane by the action of 2-chloroquinoline (1 mol.) on quinaldine (1·5—2 mols.) at 180—210°. It dissolves in cold organic media, giving colourless solutions which become intensely yellowish-red when warmed and exhibit two absorption bands in the green. On treatment with a small quantity of acid, the alcoholic solution becomes wine-red, resembling a solution of ψ-*iso*cyanine, but is ultimately decolorised by an excess of acid. The mother-liquors from the crystallisation of di-2-quinolylmethane gradually deposit the labile *isomeride*, $C_{10}H_6N{\cdot}CH{:}C_{10}H_6{:}NH$, long, bright red needles which become somewhat paler at 95° and have m. p. 103° (mixed m. p. 102—103)°. With acids, it exhibits the same behaviour as the colourless modification. Di-2-quinolylmethane yields a *dipicrate*, yellow crystals, m. p. 210° (decomp.) and a *monopicrate*, (+MeOH), matted red needles, decomp. 239° (*tri-2-quinolylmethane monopicrate* forms blackish-violet needles, decomp. 239°). *Di-2-quinolylmethane methiodide*, $C_{21}H_{20}N_2I_2$, orange-red prisms, decomp.

about 205°, is converted by alkali into N-*methyl-2-quinolylene-quinaldine*, $C_{10}H_6N{\cdot}CH{:}C_{10}H_6NMe$, red, hexagonal plates with metallic reflex, m. p. 156°, which is preferably obtained by heating di-2-quinolylmethane with an exactly equimolecular quantity of methyl sulphate. The substance only yields a *monopicrate*, dark red, metallic leaflets, decomp. 184°, even when an excess of picric acid is used. The presence of one double bond capable of yielding additive compounds is proved by titration with bromine.

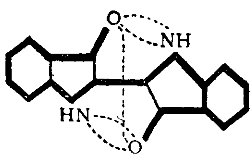
The synthesis of ψ-*iso*cyanine is effected by heating *N*-methyl-2-quinolylenequinaldine with an excess of methyl sulphate and isolation of the dye through the iodide; in substance and as the picrate it is identical with ψ-*iso*cyanine prepared in the usual manner, thus affording further evidence in favour of the formula,

$$C_{10}H_6NMe{:}CH{\cdot}C_{10}H_6NMeI,$$

advanced previously for the compound by Fischer and Scheibe (this vol., i, 56).

Quinoline-red is synthesised by heating di-2-quinolylmethane with an excess of benzylidene chloride at 100° and subsequent treatment of the product with pyridine at 150—160°. As thus prepared, the substance is identical with that derived from quinoline, quinaldine, and benzotrichloride in the presence of zinc chloride (compare Vongerichten and Homann, A., 1913, i, 99). H. W.

The Constitution of Indigotin. R. ROBINSON (*J. Soc. Dyers and Col.*, 1921, **37**, 77—81).—The manner in which partial valency formulæ may be employed to symbolise the properties and relations of chemical individuals more accurately than is possible with expressions involving normal valencies only is exemplified in the case of indigotin. The view is adopted that colour intensification by auxochromes is due to the making and breaking of partial valencies. The analogy between indigotin and indanthrene is very close, and that the cause of the colour resides in the interactions of the nitrogen atoms and the oxygen of the quinone groups is rendered very probable when the variations caused in each series by exchanging S and O for one or both of the NH-groups are considered. In both indigotin (I) and indanthrene (II) there is a double possibility of partial valency union between quinonoid oxygen and the auxochrome nitrogen :—



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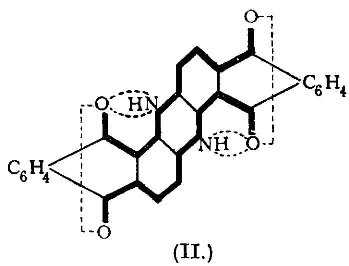
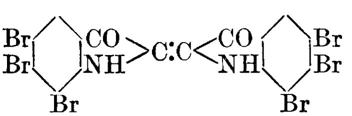


(II.)

These formulæ express this view of the origin of colour, and at the same time fully symbolise the chemical properties of these compounds. F. M. R.

Halogenated Nitrobenzaldehydes and Halogenated Indigotins. L. C. JANSE (*Rec. trav. chim.*, 1921, **40**, 285—317).—*p*-Aminobenzaldehyde, when brominated in solution either in dilute hydrochloric acid or glacial acetic acid, gives an almost quantitative yield of 3 : 5-dibromo-4-aminobenzaldehyde. The amino-group in the latter compound may be replaced more or less readily by chlorine, bromine, iodine, or hydrogen atoms, and the products on nitration yield halogenated *o*-nitrobenzaldehydes, which with acetone in the presence of alkali give halogenated indigotins.

p-Aminobenzaldehyde gives a *semicarbazone*, m. p. 173°; and its acetyl derivative gives an *azine*, $N_2(:CH{\cdot}C_6H_4{\cdot}NHAc)_2$, m. p. 309—310°, and a *semicarbazone*, m. p. 214°. 3 : 5-Dibromo-4-aminobenzaldehyde gives an *azine*, a *phenylhydrazone*, m. p. 147°; an *oxime*, m. p. 164°, and a *semicarbazone*, m. p. 294°. When this amine was diazotised and the product submitted to the Sandmeyer reaction, the amino-group was replaced as indicated above. 3 : 4 : 5-Tribromobenzaldehyde gave an *azine*, m. p. 315°; a *phenylhydrazone*, m. p. 158°; an *oxime*, m. p. 172°, and a *semicarbazone*, m. p. 314°. On nitration, it yielded 3 : 4 : 5-*tribromo*-2-*nitrobenzaldehyde*, m. p. 154°, which gave an *azine*, m. p. 309°; a *phenylhydrazone*, m. p. 218°; an *oxime*, m. p. 171°; and a *semicarbazone*, m. p. 205°; and on oxidation with alkaline potassium permanganate solution, 3 : 4 : 5-*tribromo*-2-*nitrobenzoic acid*, m. p. 264°. When dissolved in acetone and submitted to the action of sunlight tribromonitrobenzaldehyde gave 3:4:5-*tribromo*-2-*nitrosobenzoic acid*, m. p. 196°, but when to the acetone solution as soon as prepared *N*/10-sodium hydroxide was added 5:6 : 7 : 5′ : 6′ : 7′-*hexabromoindigotin* (annexed formula) was obtained.



3 : 5-Dibromobenzaldehyde gave an *azine*, m. p. 259°; a *phenylhydrazone*, m. p. 122°; an *oxime*, m. p. 123°, and a *semicarbazone*, m. p. 238°; and on nitration yielded 3 : 5-*dibromo*-2-*nitrobenzaldehyde*, m. p. 133°, and in some cases a small amount of 3 : 5-*dibromo*-4-*nitrobenzaldehyde*, m. p. 166°. 3 : 5-Dibromo-2-nitrobenzaldehyde gave an *azine*, m. p. 286°; a *phenylhydrazone*, m. p. 190°; an *oxime*, m. p. 102°, and a *semicarbazone*, m. p. 236°. Its acetone solution, when submitted to sunlight, yielded 3 : 5-*dibromo*-2-*nitrosobenzoic acid*, m. p. 209°, but when treated with *N*/10-sodium hydroxide yielded 5 : 7 : 5′ : 7′-tetrabromoindigotin.

3 : 5-*Dibromo*-4-*chlorobenzaldehyde*, m. p. 107°, on oxidation gave 3 : 5-*dibromo*-4-*chlorobenzoic acid*, m. p. 235°, and on nitration 3 : 5-*dibromo*-4-*chloro*-2-*nitrobenzaldehyde*, m. p. 125°, which in acetone solution with *N*/10-sodium hydroxide yielded 5 : 7 : 5′ : 7′-*tetrabromo*-6 : 6′-*dichloroindigotin*.

3 : 5-*Dibromo*-4-*iodobenzaldehyde*, m. p. 131°, on nitration gave 3 : 5-*dibromo*-4-*iodo*-2-*nitrobenzaldehyde*, m. p. 186°, which yielded 5 : 7 : 5′ : 7′ *tetrabromo*-6 : 6′-*di-iodoindigotin*.

A number of the azines, oximes, and semicarbazones described above crystallised with a half, one, or two molecules of water.

W. G.

Derivatives of *m*-Xylene. SIDNEY ALBERT PEARMAN (T., 1921, **119**, 717—721).

4-β-Methylaminoethylglyoxaline. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1921, **119**, 734—740).

Preparation of 5(4)-Arylalkylaminoalkylglyoxalines of the General Formula $C_3H_3N_2\cdot[CH_2]_x\cdot NH\cdot[CH_2]_x\cdot$Aryl. OTTO GERNGROSS (D.R.-P. 332955; from *Chem. Zentr.*, 1921, ii, 806. Compare A., 1915, i, 29, and A., 1915, i, 167).—Chloroalkylglyoxalines of the general formula $CH_2Cl\cdot[CH_2]_x\cdot C_3H_3N_2$ and arylalkylamines or arylalkyl chlorides of the general formula Aryl$\cdot[CH_2]_x\cdot$Cl and aminoalkylglyoxalines or the salts of these compounds are allowed to react with each other. By the action of 4-methyl-5-chloromethylglyoxaline hydrochloride on β-phenylethylamine, the secondary 5-*phenylethylaminomethyl*-4-*methylglyoxaline* and tertiary β-*phenylethylaminodi*(4-*methyl*-3-*methylglyoxaline*) are obtained which are separated by fractional crystallisation of the picrates from acetone. The *picrate* of the secondary base,

$$CH_2Ph\cdot CH_2\cdot NH\cdot C_5H_7N_2,2C_6H_3O_7N_3,$$

m. p. 208°, forms needles from hot glacial acetic acid or thick plates from acetone; the *hydrochloride* crystallises in plates, m. p. 249°, the *aurichloride*, m. p. 212°, forms yellow plates. The *picrate* of the tertiary base, $CH_2Ph\cdot CH_2\cdot N(CH_2\cdot C_3H_2N_2Me)_2,3C_6H_3O_7N_3$, m. p. 174°, forms spangles from hot glacial acetic acid containing picric acid. By heating β-4-aminoethylglyoxaline with β-*p*-hydroxyphenylethyl chloride for twelve hours in dry methyl alcohol under pressure at 100°, 4(5)-*p*-*hydroxyphenylethylaminoethylglyoxaline*, $OH\cdot C_6H_4\cdot[CH_2]_2\cdot NH\cdot[CH_2]_2\cdot C_3H_3N_2$, m. p. 156°, is obtained. The *picrate* has m. p. 201°, and forms orange-red prisms and needles. The *dihydrochloride* has m. p. 199°, spikes from boiling alcohol. Which group is in the 4-, which in the 5-position in all these compounds is uncertain. G. W. R.

Alkyl- and Acyl-barbituric Acids. HEINRICH BILTZ and HERBERT WITTEK (*Ber.*, 1921, **54**, [*B*], 1035—1058).—A general synthesis of alkylbarbituric acids is described which resembles Grimaux's method in that it depends on the use of malonic acid and the requisite carbamide, but differs from it in that phosphoryl chloride is replaced by acetic anhydride as condensing agent under specified conditions. A similar method appears to have been utilised by Wood and Anderson (T., 1907, **95**, 979). The conditions necessary for success appear to consist in the avoidance of an excess of carbamide and gradual addition of the anhydride to a solution of the other components in glacial acetic acid; the quantity of anhydride should correspond approximately with that of the water liberated during the reaction.

The preparation of the following acids in this manner is described, the yields being enclosed within brackets. Barbituric acid, m. p. 245° and decomp. 260° after resolidification (more than 70%); 1-methylbarbituric acid, m. p. 132° (nearly 70%); 1 : 3-dimethylbarbituric acid, m. p. 123° (nearly 75%); 1-*ethylbarbituric acid*,

rectangular leaflets, m. p. 119—120° (70%); 1 : 3-diethylbarbituric acid, m. p. 52° (80%).

Barbituric, 1-methylbarbituric, and 1 : 3-dimethylbarbituric acids are converted by diazomethane into the same *trimethylbarbituric acid*, which consequently has the constitution indicated by the formula $NMe<\genfrac{}{}{0pt}{}{CO-CH}{CO\cdot NMe}>C\cdot OMe$; it crystallises in long, colourless needles, m. p. 165°.

The following derivatives of 1-ethylbarbituric acid, prepared by the usual methods, are described. 1-*Ethylvioluric acid* and its *monohydrate*, decomp. 183°; *carbamide* 1-*ethylviolurate*, slender needles, decomp. 148°. 5 : 5-*Dichloro*-1-*ethylbarbituric acid*, colourless lustrous prisms, m. p. ($+H_2O$) 140—143° after much softening at 138°, m. p. (anhydrous) 141—144°. 5 : 5-*Dibromo*-1-*ethylbarbituric acid*, m. p. 123—124°, *monohydrate*, acute prisms, m. p. about 86°. 5-*Bromo*-1-*ethylbarbituric acid*, m. p. 96° to a turbid liquid which becomes transparent at 103—104°, *dihydrate*, small coarse prisms, m. p. about 86—87°; *ammonium* salt, prisms or long, colourless crystals, decomp. about 150°. 5-*Chloro*-1-*ethylbarbituric acid* and its *dihydrate*, prisms, m. p. 146—151° after softening from 90°, 1-*ethyluramil*, colourless leaflets, decomp. 230°. 1-*Ethyl-ψ-uric acid*, leaflets, decomp. 218° after gradual darkening from about 100°. 1-*Ethyluric acid*, pointed leaflets, decomp. 350° after darkening from about 335°.

Acetylbarbituric acid is obtained as by-product of Grimaux's synthesis of barbituric acid from malonic acid and carbamide, the acetic acid being derived from the decomposition of part of the malonic acid. The product has been regarded as 5-acetylbarbituric acid by Conrad and Guthzeit, who, however, do not bring forward any experimental evidence on the point. The correctness of the supposition, however, is confirmed by the later synthesis of a similar product from 1 : 3-diethylbarbituric acid and the possibility of the tautomeric structure $NH<\genfrac{}{}{0pt}{}{CO\cdot CH}{CO\cdot NH}>C\cdot OAc$ is now excluded, since it is found that the substance has all the properties of a ketone and, further, cannot be hydrolysed.

The synthesis described above can be modified in such a manner that it yields acetylbarbituric acids by using acetic anhydride in greater concentration. The products can also be obtained by warming barbituric acids with acetic anhydride.

5-Acetylbarbituric acid, minute, colourless, crystalline needles, m. p. 296—300° (decomp.), is prepared in nearly 85% yield by the gradual addition of carbamide to a solution of malonic acid in freshly-distilled acetic anhydride; a few drops of concentrated sulphuric acid are added, after which the mixture is cautiously heated to its boiling point and maintained at this temperature for some time. It is readily converted by bromine into 5 : 5-dibromobarbituric acid, large, rectangular plates, m. p. 234°. It yields an *oxime*, thin leaflets, m. p. 243° (decomp.), and a *phenylhydrazone*, colourless needles, m. p. 308—310° (decomp.). 5-*Acetyl*-1-*methylbarbituric acid*, rhombic leaflets, m. p. 207° (decomp.), gives an

oxime, needles, m. p. 211—212° (decomp.), a *phenylhydrazone*, needles, m. p. 223° (decomp.), and a *hydrazone*, long needles, m. p. 254° (decomp.); it is converted by bromine and water into 5 : 5-dibromo-1-methylbarbituric acid, acute prisms, m. p. 114°. In a similar manner, 5-*acetyl*-1 : 3-*dimethylbarbituric acid*, almost colourless, rhombic leaflets, m. p. 195° [*ammonium* salt, small, colourless needles, m. p. about 167° (decomp.)], gives an *oxime*, long, flattened prisms, m. p. about 145°; a *phenylhydrazone*, quadratic or hexagonal leaflets, m. p. 182°, and a *semicarbazone*, small, colourless prisms, m. p. 241°, and is convertible into 5 : 5-dibromo-1 : 3-dimethylbarbituric acid, m. p. 172—173°. 5-*Acetyl*-1-*ethylbarbituric acid*, slender needles, m. p. 162—163°, is transformed into its *oxime*, needles, m. p. about 188—190° (decomp.), after softening at 185°, *phenylhydrazone*, colourless, hexagonal leaflets, m. p. 210—211° (decomp.), *semicarbazone*, colourless needles, m. p. about 242—245° (decomp.), and into 5 : 5-dibromo-1-ethylbarbituric acid, m. p. 124°. 5-*Acetyl*-1 : 3-*diethylbarbituric acid*, m. p. 61—62°; its *oxime*, rhombic platelets, m. p. 159°; *phenylhydrazone*, four-sided leaflets, m. p. 125°, and 5 : 5-dibromo-1 : 3-diethylbarbituric acid, m. p. 85°, are also described. H. W.

Benzoylene- and Picolinoylene-benzdiazoles. A. BISTRZYCKI and ALEXANDER LECCO (*Helv. Chim. Acta*, 1921, **4**, 425—438).—Fusion together of phthalic anhydride and *o*-phenylenediamine is found to give a good yield of 1 : 2-*o*-benzoylene-1 : 3-benzdiazole (compare Bistrzycki, A., 1890, 969; 1891, 746; Thiele and Falk, A., 1906, i, 750; Rupe, Thiess, and Wetter, A., 1910, i, 71; Lieb, A., 1919, i, 174), and the same method is applicable to the condensation of *o*-phenylenediamine with tetrachlorophthalic acid and with quinolinic acid.

1 : 3-Benzdiazole-2-benzamide, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}C{<}^{N-}_{NH}{>}C_6H_4$ (compare Lieb, *loc. cit.*), has m. p. 264° (decomp.). The corresponding *anilide*, $C_{20}H_{15}ON_3$, forms bundles of long, microscopic, colourless needles, m. p. about 327° (decomp.); the *hydrazide*, $C_{14}H_{12}ON_4$, colourless needles, m. p. 293° (decomp.); the phenylhydrazide, $C_{20}H_{16}ON_4$, m. p. 262° (decomp.) (Rupe, Thiess, and Wetter, *loc. cit.*, gave m. p. 244°).

Tetrachloro-1 : 2-o-*benzoylene*-1 : 3-*benzdiazole*, $\begin{array}{l} C_6Cl_4{\cdot}C{:}N \\ \;\;| \qquad\;\; | \\ CO{-}N{\cdot}C_6H_4 \end{array}$, prepared from tetrachlorophthalic acid and *o*-phenylenediamine, crystallises in thin, microscopic, greenish-yellow prisms, m. p. 290—291°, and dissolves in concentrated sulphuric acid, giving a greenish-yellow solution with a brown tinge.

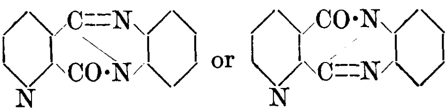
1 : 3-*Benzdiazole*-2-*tetrachlorobenzoic acid*,

$$CO_2H{\cdot}C_6Cl_4{\cdot}C{<}^{N-}_{NH}{>}C_6H_4,$$

obtained by the action of alcoholic alkali hydroxide on the preceding compound, forms bundles of microscopic needles, melting and undergoing reconversion into the internal anhydride at 236°. Its *phenylhydrazide*, $NHPh{\cdot}NH{\cdot}CO{\cdot}C_6Cl_4{\cdot}C{<}^{N-}_{NH}{>}C_6H_4$, forms

stellar aggregates of rhomb-like plates, decomposing at about 295°.

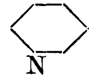
1 : 2(2′ : 3′)-*Picolinoylene*-1 : 3-*benzdiazole* (annexed formula), forms almost colourless, microscopic prisms or felted, microscopic needles, m. p. 219—220°, and dissolves in fuming hydrochloric or concentrated sulphuric acid, giving a brownish-yellow solution with a green tinge.



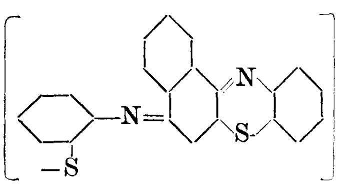
1 : 3-*Benzdiazole*-2-(3′)-*pyridine*-(2′)-*carboxylic acid*,

$$CO_2H\cdot C_5H_3N\cdot C{<}^{N}_{NH}{>}C_6H_4,$$

forms bundles of needles, m. p. 246—247° (decomp.), and exhibits faint acid and pronounced basic properties. Its *hydrochloride*, $C_{13}H_9O_2N_3$,HCl, forms silky needles, decomposing at 237°; its *methyl* ester, lustrous prisms, decomposing at 195—196°, is also markedly basic; the *amide*, $C_{13}H_{10}ON_4$, decomposes at 266° and its *anilide*, $C_{19}H_{14}ON_4$, at about 315—317°.

2-(3′)-*Pyridyl*-1 : 3-*benzdiazole*, —$C{<}^{N}_{NH}{>}C_6H_4$, obtained as a secondary product in the preparation of picolinoylenebenzdiazole from quinolinic acid and *o*-phenylenediamine, crystallises in prisms, m. p. 310°. T. H. P.

Action of *o*-Aminothiophenol on Orthoquinones. II. KNUT STAHRFOSS (*Helv. Chim. Acta*, 1921, **4**, 273—281).—Besides 5-imino-7 : 12-naphthaphenthiazine hydrochloride (A., 1920, i, 256), the interaction of *o*-aminothiophenol hydrochloride and 4-amino-1 : 2-naphthaquinone in acetic acid yields two products: (1) A phenolic compound, to be described later, and (2) a compound which is insoluble in aqueous alcoholic potassium hydroxide. This compound exhibits certain analogies to that obtained by Kehrmann (A., 1895, i, 245; 1907, i, 554) by the action of *o*-aminophenol on 4-amino-1 : 2-naphthaquinone, but, in view of its insolubility in alkali hydroxide solution and of its stability towards oxidising agents, it is regarded, not as the thiophenol, but as the disulphide corresponding with Kehrmann's compound, that is, as the disulphide (annexed formula) corresponding with *o*-mercaptophenyliminonaphthaphenthiazine. According to this structure, the compound should be obtainable directly from *o*-aminophenyl disulphide (1 mol.) and 7 : 12-naphthaphenthiazone (2 mols.), but this synthesis could not be realised; the disulphide is, however, obtained when *o*-aminophenyl disulphide (1 mol.) and 5-imino-7 : 12-naphthaphenthiazine (2 mols.) are boiled together in acetic acid solution in presence of hydrochloric acid.

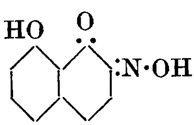


5-*Phenyliminonaphthaphenthiazine* oo-*disulphide*, $C_{44}H_{26}N_4S_4$,

forms reddish-brown needles, m. p. 285°, dissolves in most of the ordinary solvents, giving deep red solutions with pronounced red fluorescence, and at a high temperature emits violet vapours. In concentrated sulphuric acid, it dissolves to a deep red solution, which, on dilution, becomes brown and then green and deposits a green sulphate stable only in presence of excess of acid. Unlike the thiazinic disulphide prepared by Friedländer and Mauthner (A., 1905, i, 102), this disulphide is completely insoluble in sodium sulphide solution, and is not reduced by sodium hyposulphite.

Compounds which yield fluorescent solutions and otherwise exhibit analogies with the above disulphide are obtained when *o*-aminophenyl disulphide is treated with either iminonaphthaphenoxazine or iminonaphthatoluoxazine, and are to be described later. T. H. P.

1 : 8-Dihydroxynaphthalene. GUSTAV HELLER and HUGO KRETZSCHMANN (*Ber.*, 1921, **54**, [*B*], 1098—1107).—1 : 8-Dihydroxynaphthalene, m. p. 140°, is most readily prepared by heating technical 1 : 8-dihydroxynaphthalene-4-sulphonic acid with sulphuric acid and water at 150°. It couples with an equimolecular quantity of benzenediazonium chloride in hydrochloric acid solution to 4-*benzeneazo*-1 : 8-*dihydroxynaphthalene*, needles which do not melt below 260°; the same substance is formed in acetic acid or alkaline solution, but, in addition, about 10% and 7·5% of products insoluble in alkali are produced. The use of an increased proportion of diazo-compound leads, in acetic acid, but not in mineral acid solution, to the production of 4 : 5-*dibenzeneazo*-1 : 8-*dihydroxynaphthalene*, a crystalline powder, m. p. about 238°; in alkaline solution, an isomeric dibenzeneazo-dye appears also to be formed. 4-p-*Sulphobenzeneazo*-1 : 8-*dihydroxynaphthalene* forms slender, brownish-black needles; it dyes unmordanted wool dark cherry-red, a paler shade being obtained on wool mordanted with aluminium and a dark brown shade on the chrome-mordanted fibre. Attempts to prepare 4-amino-1 : 8-dihydroxynaphthalene by the reduction of the 4-benzeneazo-derivative with sodium hyposulphite in alkaline solution failed by reason of the ready oxidisability of the base, but the corresponding *tribenzoyl* compound, greyish-white leaflets, m. p. 236°, was easily prepared. Similarly, 4 : 5-diamino-1 : 8-dihydroxynaphthalene could only be isolated in the form of its *tetrabenzoyl* derivative, colourless, interwoven needles, decomp. 246°. 8-*Hydroxy*-1 : 2-*naphthaquinone*-2-*oxime* (annexed formula), brownish-yellow needles, decomp. about 183° after darkening at 170°, is prepared from molecular amounts of 1 : 8-dihydroxynaphthalene and sodium nitrite; contrary to the statements of D.R.-P. 51478, a second derivative does not appear to be produced if the proportion of the latter is increased. The quinoneoxime is converted by benzoyl chloride and sodium hydroxide into a mixture of *dibenzoyl*-8-*hydroxy*-1 : 2-*naphthaquinone*-2-*oxime*, yellow leaflets, m. p. 177° (decomp.), and 2-*nitroso*-1 : 8-*dibenzoxynaphthalene*, greyish-white leaflets, m. p. 203°



(decomp.). Reduction and subsequent benzoylation transforms the quinoneoxime into *tribenzoyl-2-amino-1 : 8-dihydroxynaphthalene*, colourless, crystalline powder, m. p. 201°.

1 : 8-*Dihydroxy-2-naphthaldehyde*, yellow needles, is prepared in 20% yield by the action of hydrogen chloride on a solution of 1 : 8-dihydroxynaphthalene and hydrocyanic acid in anhydrous ether in the presence of zinc chloride; it becomes discoloured at 110° and black at 170°. The corresponding *phenylhydrazone* does not melt below 285°.

Dibromo-1 : 8-*dihydroxynaphthalene* is obtained in colourless, unstable needles by the action of bromine in glacial acetic acid solution. 1 : 8-*Dimethoxynaphthalene* crystallises in colourless leaflets, m. p. 50°, and can be volatilised without decomposition. H. W.

Aromatic Acylamines as Azo-components. W. König and K. Köhler (*Ber.*, 1921, **54**, [*B*], 981—987).—It is shown that diazotised *p*-nitroaniline couples with *p*-toluenesulphonyl-α- and -β-naphthylamides with the formation of substances of the type $O\dot{:}N\cdot C_6H_4\cdot N\dot{:}N\cdot C_{10}H_6\cdot N\dot{:}SO\cdot C_6H_4Me$; since reaction does not occur
O ························ Na ······ O
under similar conditions with the corresponding methylnaphthylamides, it appears probable that the naphthylsulphonamide couples in its enolic form, $C_{10}H_7\cdot N\dot{:}SO(OH)\cdot C_6H_4Me$. It is also found that carboxyamides are able to couple with diazotised *p*-nitroaniline; the extreme slowness with which reaction takes place is the probable cause of the change having been overlooked previously. The auxochromic power of the different groups decreases in the order $-OH$, $-NH\cdot SO_2\cdot C_6H_4Me$, $-NHBz$, $-NHAc$.

The *sodium* salt of 4-p-*nitrobenzeneazo*-1-p-*toluenesulphonamidonaphthalene*, red needles, m. p. 210°, is obtained in good yield by the addition of *p*-nitrobenzenediazonium chloride and sodium acetate to an equivalent quantity of α-naphthyl-*p*-toluenesulphonamide. The corresponding β-naphthyl *derivative* forms long, red needles, m. p. 204°. p-*Toluenesulphonylmethyl-α-naphthylamide*, colourless leaflets, m. p. 124—125°, is prepared from *p*-toluenesulphonyl-α-naphthylamide and methyl sulphate in the presence of potassium hydroxide.

4-p-*Nitrobenzeneazo*-1-*acetylaminonaphthalene*,

$$NO_2\cdot C_6H_4\cdot N\dot{:}N\cdot C_{10}H_6\cdot NHAc,$$

slowly separates when solutions of acet-α-naphthalide in acetic acid and *p*-nitrobenzenediazonium chloride and sodium acetate are mixed and preserved at 0° for about a week; it forms brownish-red needles, m. p. 285—286°, and is identical with the product prepared by treating *p*-nitrobenzeneazo-α-naphthylamine with acetyl chloride and pyridine. 4-p-*Nitrobenzeneazo*-1-*benzoylaminonaphthalene*, which is formed even more slowly than the corresponding acetyl compound, crystallises in small, brownish-red needles, m. p. 214—215°.
H. W.

Non-aromatic Diazonium Salts. VI. 3 : 5-Dimethyl*iso*oxazole-4-diazonium Salts and their Azo-derivatives. Gilbert T. Morgan and Henry Burgess (T., 1921, **119**, 697—703).

Nitrocyanophenylhydrazines. W. Borsche (*Ber.*, 1921, **54**, [*B*], 660—669).—The experiments were undertaken with the object of elucidating the constitution of the substance, $C_{26}H_{16}ON_8$, obtained by the action of phenylhydrazine on 4-bromo-3-nitrobenzonitrile (Borsche, Stackmann, and Makaroff-Semljanski, A., 1917, i, 15).

4-Bromo-3-nitrobenzonitrile reacts readily with hydrazine hydrate in alcoholic solution to yield 3-*nitro*-4-*hydrazinobenzonitrile*, $NO_2\cdot C_6H_3(CN)\cdot NH\cdot NH_2$, slender needles, m. p. 221° (decomp.), which is converted by warm aqueous sodium hydroxide solution into 6-*cyano*-1 : 2 : 3-*benztriazole*, $CN\cdot C_6H_3<\substack{N:N \\ | \\ N\cdot OH}$, colourless needles which explode at 218—219° after becoming discoloured at 210°. The cyanide is not convertible into *ethyl* 3-*nitro*-4-*hydrazinobenzoate*, m. p. 103°, by alcoholic hydrogen chloride, but the ester is readily prepared from hydrazine hydrate and ethyl 3-bromo-4-nitrobenzoate. Boiling glacial acetic acid slowly converts the nitrile into 3-*nitro*-4-*acetylhydrazinobenzonitrile*, small, yellow needles, m. p. 203°, whilst a mixture of acetic acid and anhydride gives the *diacetyl* compound, $NO_2\cdot C_6H_3(CN)\cdot NH\cdot NAc_2$, yellow leaflets, m. p. 185°. With the requisite quantity of benzoyl chloride in boiling pyridine solution, the *mono-benzoyl* derivative, large, golden-yellow leaflets, m. p. 226—227°, and the *dibenzoyl* compound, pale yellow crystals, m. p. 173—174°, are formed. *Anisaldehyde*-2-*nitro*-4-*cyanophenylhydrazone*, blood-red needles, m. p. 239°, *acetone*-2-*nitro*-4-*cyanophenylhydrazone*, orange-yellow needles, m. p. 128—129°, and *benzophenone*-2-*nitro*-4-*cyanophenylhydrazone*, red, crystalline powder, m. p. 208—209°, are described. 2′-*Nitro*-4′-*cyano*-4-*hydroxyazobenzene*, $NO_2\cdot C_6H_3(CN)\cdot N:N\cdot C_6H_4\cdot OH$, dark brown, flattened needles, m. p. 236—237°, is readily prepared from 3-nitro-4-hydrazinobenzonitrile and *p*-benzoquinone, whereas the oxime of the latter yields p-*benzoquinoneoxime*-2-*nitro*-4-*cyanophenylhydrazone*, $NO_2\cdot C_6H_3(CN)\cdot NH\cdot N:C_6H_4:N\cdot OH$, small, dark red crystals, m. p. 229° (decomp.), which is converted by nitric acid in glacial acetic acid solution into 2′ : 4-*dinitro*-4′-*cyanoazobenzene*, pale brown, microscopic needles, m. p. 188—189°.

6-Chloro-3-nitrobenzonitrile, colourless needles, m. p. 108—109°, is converted by hydrazine hydrate into 4-*nitro*-2-*cyanophenylhydrazine*, slender, red needles, m. p. 250°; the *monoacetyl* derivative crystallises in yellow leaflets, m. p. 308°, whilst the *mono*- and *di-benzoyl* compounds form yellow needles, m. p. 223°, and pale yellow granules, m. p. 232—233°, respectively. o-*Hydroxybenzaldehyde*-4-*nitro*-2-*cyanophenylhydrazone*, small, brownish-yellow crystals, m. p. 231°, and *anisaldehyde*-4-*nitro*-2-*cyanophenylhydrazone*, slender, yellow needles, m. p. 163—165°, are described, but the hydrazine derivative could not be caused to react with acetone or acetophenone; its action towards *p*-benzoquinone or its oxime differs from that of the 2-nitro-4-cyano-compound.

6-*Nitro*-4-*cyano*-m-*tolylhydrazine*, $C_8H_8O_2N_4$, forms coarse, yellowish-red prisms, m. p. 217—218° ($+H_2O$, slender, dark red needles); the *monoacetyl* derivative crystallises in yellow leaflets, m. p.

291—292°. The hydrazine derivative reacts readily with picryl chloride to give 2′ : 4′ : 6′-*trinitrobenzenehydrazo*-6-*nitro*-4-*cyanotoluene*, $NO_2·C_6H_2Me(CN)·NH·NH·C_6H_2(NO_2)_3$, shining, red crystals, m. p. 258—259° (decomp.). The hydrazine derivative reacts only with aldehydes to yield hydrazones, but the change does not proceed smoothly, and the product is invariably more or less contaminated with azines. The latter type of substance is solely produced when benzophenone is employed. Salicylaldehyde gives a mixture of *o*-hydroxybenzylideneazine, m. p. 216°, and o-*hydroxybenzaldehyde*-6-*nitro*-4-*cyano*-m-*tolylhydrazone*, pale yellow needles, m. p. 247—248°, whilst anisaldehyde yields anisylideneazine and *anisaldehyde*-6-*nitro*-4-*cyano*-m-*tolylhydrazone*, a dark yellow, crystalline powder, m. p. 172—173°. H. W.

5-Chloro-2 : 4-dinitrophenylhydrazine and 4 : 6-Dinitro-1 : 3-dihydrazinobenzene. W. Borsche (*Ber.*, 1921, **54**, [*B*], 669—684).—The replacement of one chlorine atom of 1 : 5-dichloro-2 : 4-dinitrobenzene by the hydrazine residue has been recorded by Borsche and Bahr (A., 1914, i, 28). It is now found that the second chlorine atom can also be replaced by a variety of groups, thus leading to the production of a variety of hydrazines; the replacement is preferably effected before the introduction of the hydrazine group, since this, in the ortho-position to a nitro-group, is somewhat unstable.

5-Chloro-2 : 4-dinitrophenylhydrazine, slender, yellow needles, m. p. 198°, is prepared by the gradual addition of hydrazine hydrate to a solution of 1 : 5-dichloro-2 : 4-dinitrobenzene in boiling ethyl alcohol. It yields a *monoacetyl* derivative, slender, yellow needles, m. p. 192—193°, and a *diacetyl* compound, yellow needles, m. p. 131—132.° With *p*-benzoquinone, it gives 5-*chloro*-2 : 4-*dinitro*-4′-*hydroxyazobenzene*, brown needles, m. p. 190—191°, and with quinoneoxime it yields p-*benzoquinoneoxime*-5-*chloro*-2 : 4-*dinitrophenylhydrazone*, $C_6H_2Cl(NO_2)_2·NH·N:C_6H_4:N·OH$, small, dark red needles, decomp. 224—225°, which is converted by nitric acid in acetic acid solution into 5-*chloro*-2 : 4 : 4′-*trinitroazobenzene*, pale reddish-brown powder, m. p. 154°.

2:4-*Dinitro*-5-*hydrazinoaniline* (from 5-chloro-2 : 4-dinitroaniline and hydrazine hydrate) crystallises in reddish-brown needles, m. p. 236—237° (decomp.), and is transformed by *p*-benzoquinone into 2 : 4-*dinitro*-5-*amino*-4′-*hydroxyazobenzene*, a reddish-brown powder which decomposes gradually above 140° without melting sharply.

2 : 4-*Dinitro*-5-*hydrazinodimethylaniline* forms bright red, flattened needles, m. p. 177—178°, and is convertible into 2 : 4-*dinitro*-5-*dimethylamino*-4′-*hydroxyazobenzene*, reddish-brown needles, m. p. 216—217°, p-*benzoquinoneoxime*-2 : 4-*dinitro*-5-*dimethylaminophenylhydrazone*, a reddish-brown, crystalline powder, m. p. 227°, and 2 : 4 : 4′-*trinito*-5-*dimethylaminoazobenzene*, an orange-red powder, m. p. 214—216° after softening at 190°.

2 : 4-*Dinitro*-5-*hydrazinodiphenylamine* crystallises in orange-red needles, m. p. 197—198°.

2 : 4-*Dinitro*-5-*hydrazinophenol*, reddish-brown granules, m. p. 197° (decomp.), yields an *acetyl* derivative, $OH\cdot C_6H_2(NO_2)_2\cdot NH\cdot NHAc$, pale yellow needles, m. p. 225—226° (decomp.), and *acetophenone*-2 : 4-*dinitro*-5-*hydroxyphenylhydrazone*, slender, brown needles, m. p. 205—206°. 2 : 4-*Dinitro*-5 : 4′-*dihydroxyazobenzene* forms reddish-brown needles, m. p. 218° (decomp.) (? dibenzoyl derivative, slender needles, m. p. 166°). p-*Benzoquinoneoxime*-2 : 4-*dinitro*-5-*hydroxyphenylhydrazone* is a dark-red, crystalline powder, decomp. 213—215°, which is readily oxidised to 2 : 4 : 4′-*trinitro*-5-*hydroxyazobenzene*, red needles, m. p. 179°.

Ethyl 2 : 4-*dinitro*-5-*hydrazinophenylacetate* crystallises in slender, orange-red needles, m. p. 174°; it is converted by alkali and subsequent acidification into (?) 6-*nitro*-1 : 2 : 3-*benztriazole*-5-*acetic acid*, $CO_2H\cdot CH_2\cdot C_6H_2(NO_2)<\overset{\text{N}}{\underset{\text{N(OH)}}{}}>N$, which explodes at 244° after darkening above 200°.

Ethyl 2 : 4-*dinitro*-5-*hydrazinophenylmalonate*,

$$NH_2\cdot NH\cdot C_6H_2(NO_2)_2\cdot CH(CO_2Et)_2,$$

blood-red prisms, m. p. 104—105°, is converted by *p*-benzoquinone into *ethyl* 2 : 4-*dinitro*-4′-*hydroxyazobenzene*-5-*malonate*,

$$CH(CO_2Et)_2\cdot C_6H_2(NO_2)_2\cdot N{:}N\cdot C_6H_4\cdot OH,$$

red needles, m. p. 138°, and by *p*-benzoquinoneoxime into the *compound*, $CH(CO_2Et)_2\cdot C_6H_2(NO_2)_2\cdot NH\cdot N{:}C_6H_4{:}N\cdot OH$, red, rhombic leaflets, m. p. 188° (decomp.).

4 : 6-*Dinitro*-1 : 3-*dihydrazinobenzene*, flattened, brown needles, decomp. 246°, is prepared by the action of the requisite quantity of hydrazine hydrate on 5-chloro-2 : 4-dinitrophenylhydrazine or, preferably, on 4 : 6-dichloro-1 : 3-dinitrobenzene. The *diacetyl* derivative, $C_6H_2(NO_2)_2(NH\cdot NHAc)_2$, forms lemon-yellow needles which are completely molten at 305° after darkening at 280°. The following symmetrical *derivatives* of the hydrazine are obtained with the requisite aldehyde or ketone: $C_6H_2(NO_2)_2(NH\cdot N{:}CH_2)_2$, dark yellow needles, m. p. 247° (decomp.), after previous darkening: (?) $C_6H_2(NO_2)_2(NH\cdot N{:}CHPh)_2$, red leaflets, m. p. 302—304° (decomp.); $C_6H_2(NO_2)_2(NH\cdot N{:}CMe_2)_2$, slender, orange needles, m. p. 234—235° (decomp.) after previous softening:

$$C_6H_2(NO_2)_2(NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et)_2,$$

dark yellow, crystalline leaflets, m. p. 133—134°:

$$C_6H_2(NO_2)_2(NH\cdot N{:}CPh_2)_2,$$

small, dark yellow needles, m. p. 305° (decomp.) after darkening at about 280°. With *p*-benzoquinone, the dihydrazine gives 4 : 6-*dinitro*-1 : 3-*bis*-4′-*hydroxybenzeneazobenzene*, $C_6H_2(NO_2)_2(N{:}N\cdot C_6H_4\cdot OH)_2$, microscopic needles, m. p. 244—245° (*dibenzoyl* derivative, m. p. 180—181°), whilst with *p*-benzoquinoneoxime it yields the 4 : 6-*dinitrophenylene*-1 : 3-*dihydrazone* of p-*benzoquinoneoxime*, pale reddish-brown powder, decomp. 205°.

The *mono-acetyl* derivative of 4 : 6-dinitro-1 : 3-dihydrazinobenzene, yellow needles, m. p. 224° (decomp.), is converted by acetophenone into the *hydrazone*,

$$NHAc\cdot NH\cdot C_6H_2(NO_2)_2\cdot NH\cdot N{:}CMePh,$$

orange-red needles, m. p. 272° (decomp.).

2 : 4-*Dinitro-5-hydrazino-4′-hydroxyazobenzene*, m. p. 178—180°, is prepared by the action of hydrazine hydrate on the corresponding chloro-compound; with acetophenone, it gives the corresponding *hydrazone*, $OH\cdot C_6H_4\cdot N:N\cdot C_6H_2(NO_2)_2\cdot NH\cdot N:CMePh$, dark red granules, m. p. 224°. H. W.

Catalytic Hydrogenation of Phenylhydrazones. ALPHONSE MAILHE (*Compt. rend.*, 1921, **172**, 1107—1110).—Phenylhydrazones, when passed in a rapid current of hydrogen over reduced nickel at 180—190°, undergo hydrogenation. If they are derived from aldehydes, the products are aniline and a nitrile, with accessory formation of a small amount of amine. Thus valeraldehyde-phenylhydrazone gives aniline and *iso*valeronitrile with a little *iso*amylamine, and *iso*butaldehydephenylhydrazone gives aniline, *iso*butyronitrile, and traces of *iso*butylamine. If the hydrazones are derived from ketones, complete hydrogenation occurs, the products being aniline and a primary amine, which by partial decomposition may give some secondary amine. Acetonephenyl-hydrazone gives aniline, *iso*propylamine, and some di*iso*propylamine. Methyl propyl ketone-phenylhydrazone gives aniline, β-amino-pentane, and some di-α-methylbutylamine. W. G.

Aminohydrazines. VI. Acetophenone-*p*-aminophenyl-hydrazone and *p*-Aminophenylhydrazine. HARTWIG FRANZEN and PAUL STEINFÜHRER (*Ber.*, 1921, **54**, [*B*], 861—867. Compare A., 1918, i, 458, and previous abstracts). *Acetophenone*-p-*amino-phenylhydrazone*, pale yellow, lustrous leaflets, m. p. 134—136° (decomp.), is prepared in 65% yield by the reduction of acetophenone-*p*-nitrophenylhydrazone with sodium hyposulphite in alcoholic-ammonia solution. The product is somewhat unstable in substance and in solution. It is decomposed by hot alcoholic hydrogen chloride into acetophenone, ammonia, and *p*-phenylenediamine hydrochloride, but is not greatly affected by cold aqueous acid. It does not appear to yield a derivative of indole when its solution in xylene or cumene is boiled. The *benzylidene* derivative,

$$CMePh:N\cdot NH\cdot C_6H_4\cdot N:CHPh,$$

lemon-yellow needles, m. p. 178—180° (decomp.), m-*nitrobenzylidene* compound, a red, crystalline powder, m. p. 177—179°, and the *thiocarbanilide*, leaflets, m. p. 166—167° (decomp.), are described.

Acetophenone-*p*-aminophenylhydrazone is transformed by cold, 10% hydrochloric acid into p-*aminophenylhydrazine hydrochloride*, pale yellow, slender needles, which decomposes rapidly in solution, slowly in substance. It was not found possible to isolate the corresponding free *base* in the solid state, but its transitory presence in solution is shown by the preparation of the following derivatives : di-benzylidene-*p*-aminophenylhydrazone, $CHPh:N\cdot C_6H_4\cdot NH\cdot N:CHPh$; *di*-p-*methoxybenzylidene*-p-*aminophenylhydrazone*, a greenish-yellow, crystalline powder, m. p. 181—182°; *pyruvic acid*-p-*aminophenyl-hydrazone*, an unstable, grey powder, m. p. 145—147° (decomp.); *tribenzoyl*-p-*aminophenylhydrazine*, a grey, crystalline powder, m. p. 236—237°. H. W.

Phenylhydrazine Derivatives of Unsaturated Fatty-aromatic Ketones and the Products of their Transformation. KARL VON AUWERS and ELISABETH LÄMMERHIRT (*Ber.*, 1921, **54**, [*B*], 1000—1024).—It is shown that ketones of the type Ph·CO·CH:CHR give pyrazolines with free hydrazines, whilst those of the class CRR′:CH·CO·C_6H_4·OH yield either monohydrazino-derivatives or hydrazino-hydrazones. The latter are readily oxidised to azo-compounds and are degraded by boiling dilute acetic acid to hydrazones of *o*-acetylphenols. The *p*-nitrophenylhydrazone of *p*-hydroxy-*o*-tolyl *iso*butenyl ketone is converted into a pyrazoline or a chromanone, according to experimental conditions.

Contrary to Kohler's statement (A., 1909, i, 938), 5-methyl-1 : 3-diphenylpyrazoline, $CH_2<\begin{matrix}CHMe\cdot NPh\\ CPh=\!=N\end{matrix}$, m. p. 104—105° (Kohler gives m. p. 108°), is slowly formed from an alcoholic, acetic acid solution of propenyl phenyl ketone and phenylhydrazine at the laboratory temperature. With *p*-nitrophenylhydrazine hydrochloride, the ketone forms *phenyl propenyl ketone*-p-*nitrophenylhydrazone*, small, reddish-brown prisms, m. p. 151—152°, the constitution of which is deduced from the production of *p*-phenylenediamine on reduction and the absence of Knorr's pyrazoline reaction. *iso*Butenyl phenyl ketone appears to yield a normal phenylhydrazone with a molecular amount of phenylhydrazine, and (?) 1 : 3-*diphenyl*-5 : 5-*dimethylpyrazoline* with a double proportion of the reagent. *p*-Crotonylanisole and phenylhydrazine in alcohol–acetic acid solution give 1-*phenyl*-3-p-*anisyl*-5-*methylpyrazoline*, colourless, lustrous leaflets, m. p. 137—138°, whilst propenyl *p*-tolyl ketone, when similarly treated, yields 1-*phenyl*-3-p-*hydroxy*-o-*tolyl*-5-*methylpyrazoline*, pale yellow, silky needles, m. p. 122·5—123°; this substance is also obtained when an excess of phenylhydrazine and a more concentrated acid are used.

The *phenylhydrazone* of β-*phenylhydrazino*iso*butyl* p-*hydroxy*-o-*tolyl ketone*, OH·C_6H_3Me·C(:N·NHPh)·CH_2·CMe_2·NH·NHPh, is obtained when the ketone (1 mol.) and phenylhydrazine (2 mols.) are allowed to react in alcohol–acetic acid solution at the laboratory temperature or when an alcoholic solution of the components is heated to boiling during some hours; it forms pale yellow prisms, m. p. 139—141°, and is oxidised by air, more readily by ferric chloride, hydrogen peroxide, or mercuric oxide, to β-*benzeneazo*iso*butyl* p-*hydroxy*-o-*tolyl ketone phenylhydrazone*, OH·C_6H_3Me·C(:N·NHPh)·CH_2·CMe_2·N:NPh, slender, orange-yellow needles, m. p. 123—124°. The former compound is transformed by hot glacial acetic acid or, more slowly, by a mixture of equal volumes of alcohol and glacial acetic acid into the phenylhydrazone of *o*-acetyl-*p*-cresol, m. p. 154—155° (the azo-compound is unaffected by the latter treatment), but the fate of the residue, ·$C(CH_3)_2$·NH·NHPh, could not be decided; it was not possible to detect the presence of acetone, phenylhydrazine, or acetonephenylhydrazone. Closely similar observations are recorded with *p*-bromophenylhydrazine. β-p-*Bromophenylhydrazino*iso*butyl* p-*hydroxy*-o-*tolyl ketone* p-*bromophenylhydrazone* crystallises in small, pale yellow, lustrous prisms, m. p. 167—170°. It is readily oxidised

by ferric chloride in boiling alcoholic solution to β-p-*bromobenzeneazo*iso*butyl* p-*hydroxy*-o-*tolyl ketone* p-*bromophenylhydrazone*, lustrous, orange-coloured needles, m. p. 145—146°, and is converted by a boiling mixture of alcohol and glacial acetic acid, but not by the former solvent alone, into the p-*bromophenylhydrazone* of o-*acetyl*-p-*cresol*, coarse, pale yellow prisms, m. p. 185—186°.

With *p*-nitrophenylhydrazine or its hydrochloride, the reaction follows a different course. A bi-derivative could not be obtained from the free base, and the ketone reaction leading at the atmospheric or slightly higher temperature to a compound of equimolecular proportions of the components; in one instance, a yellow substance, m. p. 125—126°, was isolated, but all subsequent experiments led to the production of β-p-*nitrophenylhydrazino*iso*butyl* p-*hydroxy*-o-*tolyl ketone*, $OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$, coarse, brownish-yellow prisms, m. p. 158°, which is readily oxidised by ferric chloride to β-p-*nitrobenzeneazo*iso*butyl* p-*hydroxy*-o-*tolyl ketone*, small, orange-red prisms, m. p. 76—77°. The two substances exhibit a very different behaviour towards *p*-nitrophenylhydrazine hydrochloride, which is without action on the former in boiling alcoholic solution, but converts the latter into β-p-*nitrobenzeneazo*iso*butyl* p-*hydroxy*-o-*tolyl ketone* p-*nitrophenylhydrazone*, dark red crystals, m. p. 213—215°. The indifference of the former is analogous to the behaviour of the corresponding semicarbazido-compound towards semicarbazide (following abstract). The action of free *p*-nitrophenylhydrazine on the ketone in boiling alcoholic solution leads to the production, amongst other substances, of the *p*-nitrophenylhydrazone of *o*-acetyl-*p*-cresol, even in the absence of acetic acid. On the other hand, *p*-nitrophenylhydrazine hydrochloride converts the ketone in cold solution into the simple p-*nitrophenylhydrazone*, brownish-red, flattened needles, m. p. 163—165°, 164—168° and 166—170° for different preparations, and this is the sole product even in the presence of an excess of the hydrazine salt. Since an additive product is not formed, the side-chain does not become shortened when an alcoholic solution of the ketone is boiled with *p*-nitrophenylhydrazine hydrochloride; in these circumstances, however, a mixture of the *p*-nitrophenylhydrazone of 2 : 2 : 6-trimethylchromanone, $O<\begin{matrix}C_6H_3Me\cdot C{:}N\cdot NH\cdot C_6H_4\cdot NO_2\\ CMe_2{-\!-}CH_2\end{matrix}$, red crystals, m. p. 202°, and (?) 5 : 5-*dimethyl*-1-p-*nitrophenyl*-3-p-*hydroxy*-o-*tolylpyrazoline*, $OH\cdot C_6H_3Me\cdot C<\begin{matrix}N{-\!-}N\cdot C_6H_4\cdot NO_2\\ CH_2\cdot CMe_2\end{matrix}$, slender, yellow needles, m. p. 210—211°, is produced. Under the selected conditions, therefore, the nitrophenylhydrazone becomes isomerised in two directions, yielding either the chromanone or the pyrazoline. The conditions underlying these changes have been further studied with the preformed substance. The pyrazoline is smoothly obtained by the action of alcohol containing a few drops of hydrochloric acid, but the hydrazone is unaffected by boiling alcohol or acetone at 100°. Alkali hydroxide, which readily causes the conversion of the ketone into the chromanone (Auwers and Lämmerhirt, A., 1920, i, 392), transforms the hydrazone into the pyrazoline, whereas glacial acetic

acid, which does not isomerise the ketone, converts the hydrazone into the corresponding chromanone derivative. The oxime of *p*-hydroxy-*o*-tolyl *iso*butenyl ketone is unaffected by alkalis. H. W.

The Action of Semicarbazide on Unsaturated Ketones. K. von Auwers (*Ber.*, 1921, **54**, [*B*], 987—1000).—The investigations of Rupe and his co-workers (A., 1904, i, 144; 1908, i, 12; 1910, i, 15) appear to indicate that only unsaturated ketones of the fatty series are capable of yielding semicarbazidesemicarbazones, and that this property is not shared by hydroaromatic or phenylated ketones. With regard to the latter, the statement is in need of restriction; Rupe's observations were made with ketones of the type CHPh:CH·CO·R, but, as is now shown, the formation of semicarbazidesemicarbazones occurs with relative smoothness and rapidity with substances of the class COPh·CH:CHR.

Phenylpropenyl ketone reacts with semicarbazide hydrochloride and sodium acetate in aqueous alcoholic solution at the ordinary temperature with the formation of the *semicarbazone* of *phenyl β-semicarbazidopropyl ketone*,

$$NH_2·CO·NH·N:CPh·CH_2·CHMe·NH·NH·CO·NH_2,$$

a colourless, crystalline powder, m.p. 191—192° (decomp.). p-*Anisylpropyl ketone semicarbazidesemicarbazone* has m. p. 159—160°. Similarly, *p*-methoxy-*o*-tolyl propenyl ketone, b. p. 156—161°/13 mm., gives a *semicarbazidesemicarbazone*, m. p. 205—206°, whilst the similar *compound* from *p*-hydroxy-*o*-tolyl propenyl ketone has m. p. 200—201°. All the substances are basic in character and relatively readily soluble in water; they are rather more stable than Rupe's substances, and are not noticeably affected by short boiling with alcohol or water.

The action of ββ-dimethylacrylyl chloride on benzene in the presence of aluminium chloride and carbon disulphide has been examined with the hope of readily obtaining phenyl *iso*butenyl ketone. Contrary to expectation, however, the product of the change is 3 : 3-*dimethyl*-1-*hydrindone*, $C_6H_4<\substack{CMe_2\\ -CO-}>CH_2$, a colourless liquid, b. p. 130—131°/18 mm., $D_4^{14\cdot25}$ 1·0320, D_4^{20} 1·027, $n_\alpha^{14\cdot25}$ 1·54026, $n_D^{14\cdot25}$ 1·54525, $n_\beta^{14\cdot25}$ 1·55936, $n_\gamma^{14\cdot25}$ 1·57182, n_D^{20} 1·5427. Its *semicarbazone* crystallises in slender, lustrous needles, m. p. 205—207°, after previous softening. The constitution of the hydrindone derivative is established by its synthesis from β-bromo*iso*valeryl chloride and aluminium chloride.

The behaviour of *p*-hydroxy-*o*-tolyl *iso*butenyl ketone appears to be abnormal, since it only yields p-*hydroxy*-o-*tolyl β-semicarbazido*-iso*butyl ketone*, $OH·C_6H_3·Me·CO·CH_2·CMe_2·NH·NH·CO·NH_2$, silky needles, m. p. 148—149°, even in the presence of an excess of semicarbazide, the accumulation of substituents at the β-carbon atom appearing to restrict the reactivity of the carbonyl group. This is not, however, true of all reagents, since the semicarbazido-derivative readily yields the corresponding *oxime*, m. p. 202—203°, whilst the parent substance behaves normally towards hydroxylamine, giving the *oxime*, $OH·C_6H_3Me·C(:N·OH)·CH:CMe_2$, small glassy prisms,

m. p. 130·5—131·5°, with hydroxylamine hydrochloride and the additive *compound*, $OH{\cdot}C_6H_3Me{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}NH{\cdot}OH$, coarse, colourless crystals, m. p. 139—140°, with the free base.

Phenyl propenyl ketone has b. p. 122—123°/12 mm., $D_4^{18\cdot3}$ 1·0298, D_4^{20} 1·028, $n_\alpha^{18\cdot3}$ 1·55465, $n_D^{18\cdot3}$ 1·56091, $n_\beta^{18\cdot3}$ 1·57896, $n_\gamma^{18\cdot3}$ 1·59544, n_D^{20} 1·5601. It is smoothly converted by bromine in carbon disulphide solution into αβ-dibromobutyrophenone, m. p. 98—99°, whereas Kohler, who prepared it from αβ-dibromobutyryl chloride and benzene, gives m. p. 112° (A., 1909, i, 938). Repetition of the latter work yielded a product, m. p. 98—99°, and gave αβ-dibromobutyryl chloride, b. p. 78—85° (mainly 82·5°)/12 mm., whereas Kohler gives b. p. 112°/20 mm. H. W.

Preparation of Fibrinogen. J. McLean (*Bull. Johns Hopkins Hosp.*, 1920, **31**, 453; from *Physiol. Abstr.*, 1921, **6**, 12).—Fibrinogen, salted out by sodium chloride, is often difficult to dissolve. Ammonium sulphate ($\frac{1}{4}$ volume of saturated solution added to centrifugalised oxalated plasma) gives a more soluble product, more free from prothrombin. G. B.

Action of Sodium Hydroxide on the Coagulation of Fibrinogen. John Oglethorpe Wakelin Barratt (*Biochem. J.*, 1921, **15**, 1—10).—The retarding action of sodium hydroxide on the coagulation of fibrinogen in the presence of thrombin is due to a gradual disappearance of the fibrinogen, and not to an effect on the thrombin. The fibrin fibrils diminish in size and number, become amicroscopic, yielding a structureless gel, and finally coagulation does not take place at all. G. B.

Hæmocyanin. I. Refractive Index. II. Colloidal Properties and Isoelectric point. G. Quagliariello (*Arch. Sci. Biol.*, 1920, i, 246—258; *Atti R. Accad. med. chir. Napoli*, 1920, 74; from *Physiol. Abstr.*, 1921, **6**, 12).—I. One per cent. of hæmocyanin dissolved in water increases its refractive index by 0·00197, and as the increase is proportional to the concentration, amounts of hæmocyanin up to 2% can thus be estimated. II. Hæmocyanin is completely precipitated by dialysis (the process may take thirty days) and is therefore more like a globulin than an albumin. It can in part be precipitated from blood by dilution with distilled water. One per cent. solutions of dialysed hæmocyanin are not coagulated by heat or by alcohol. Sodium chloride and sulphate partly, magnesium and ammonium sulphates completely, precipitate it. G. B.

Extraction of Melanin from Skin with Dilute Alkali. William John Young (*Biochem. J.*, 1921, **15**, 118—122).—The pigment is soluble in *N*/20 alkali hydroxide and acid; on boiling the alkaline solution, it gradually loses a little hydrogen and nitrogen and ceases to be soluble in acids. The analyses show considerable variation, but the carbon content is now found to be about 56%, and there is no iron (compare A., 1914, i, 1204). G. B.

The Theory of Invertase Action. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1921, **115**, 269—281).—Concerning the nature of enzyme action, some investigators try to apply the kinetics of homogeneous solutions to the utmost, others postulate adsorption compounds and reject the application of the law of mass action. In the case of invertase, the author wishes to combine both views and clear up an apparent contradiction. He has confirmed the quantitative experiments of Meyerhof with ferric hydroxide (A., 1914, ii, 450; compare similar experiments with charcoal by Eriksson, A., 1911, i, 698, and by Nelson and Griffin, A., 1916, i, 439, 516). Invertase adsorbed by colloidal ferric hydroxide cannot be removed by washing with water, but is slowly removed by sucrose, maltose, and raffinose, but not by lactose, dextrose, fructose, mannose, or α- or β-methylglucoside, and this removal has therefore nothing to do with ferment action. Invertase adsorbed on ferric hydroxide is evidently colloidal, yet its activity is quite unimpaired, so that the application to it of the kinetics of a homogeneous system (Michaelis and others, A., 1911, i, 1052; 1913, i, 540; 1920, i, 896) still holds good. The molecules of invertase adsorbed on ferric hydroxide must all be on the surface and all equally active (compare similar experiments on the adsorption of amylase by Ambard, this vol., i, 368). G. B.

The Co-ferment (Complement) of Diastase. W. BIEDERMANN (*Fermentforsch.*, 1920—1921, **4**, 258—300).—Animal as well as plant diastases consist of a thermolabile and by itself inactive component (zymogen) and a thermostable co-ferment such as an inorganic salt. Many experiments were made on the effect of these salts on the fermentation and also on the influence of the reaction of the solution. It was found difficult to obtain by dialysis a completely inactive diastase solution, as traces of salts were sufficient to activate the ferment. The salts used as activators were neutral salts of the alkali and alkaline-earth metals, with inorganic and organic acids, phosphates, hydrogen carbonates, and thiocyanates. The anion proved to be the active component. The most active salt was sodium chloride, closely followed by potassium thiocyanate; in the second rank were potassium chloride and bromide, sodium bromide, and ammonium chloride; in the third rank were the chlorides of calcium, magnesium, strontium, and barium. After these came nitrates, iodides, and sulphates. Of the kations, sodium had the most influence, followed by potassium. All the salts form with diastase complex compounds of indefinite composition which are easily dissociated. The activity of these neutral salt-diastases is greatest in strictly neutral solutions; the slightest addition of acid or alkali is enough to check fermentation at once, and with long contact the ferment is destroyed. Alkaline and acid salts behave differently from neutral salts. Sodium hydrogen phosphate and sodium hydrogen citrate in solutions up to 0·3% strength activate salt-free diastase in spite of the acid reaction of the solution; above this strength the reaction is checked. Disodium phosphate and sodium hydrogen carbonate

activate fermentation in concentrations in which more acid salts would inhibit. There is a relatively slight retardation produced by disodium hydrogen phosphate which can be removed at once by a trace of sodium chloride, the reaction remaining neutral. The diastatic power of this mixture exceeds that of all others. A slight addition of a diphosphate to a sodium chloride solution greatly increases the activating power of the latter. Sodium carbonate also has no retarding effect on an active sodium chloride-diastase. Saliva yields a diastase solution which depends for its activity on the nature of the co-ferment, that is, the inorganic salts, the most important of which are sodium chloride, potassium thiocyanate, and phosphate, to which must be added sodium hydrogen carbonate and carbon dioxide, which play an important part in the diastatic fermentation of pancreatic juice. J. H. J.

Action of Emulsin on Galactose in Solution in Propyl Alcohol of Different Strengths. MARC BRIDEL (*Compt. rend.*, 1921, **172**, 1130—1132. Compare A., 1913, i, 498, 1045).—β-Galactosidase, a ferment contained in emulsin, is killed fairly rapidly at 30° in aqueous propyl alcohol containing 10—45 grams of alcohol in 100 c.c., but is resistant in stronger alcohol. At the ordinary temperature, it remains active even in the more dilute alcohol. The yield of propyl β-galactoside increases at first with the concentration of the alcohol, but diminishes in alcohol containing 45—55 grams of alcohol per 100 c.c. because of the destruction of the enzyme. In stronger alcohol a further increase in the yield is noted, and 80% of the galactose is combined in an alcohol containing 75 grams of alcohol in 100 c.c. W. G.

A Peculiar Modification of Amygdalinase and Amygdalase due to Ageing. GABRIEL BERTRAND and ARTHUR COMPTON (*Bull. Soc. chim.*, 1921, [iv], **29**, 229—237).—Under the influence of time, both amygdalinase and amygdalase, as extracted from almonds, lose their activity very slowly to the extent of about one-third in ten years, but they show a marked variation in the optimum hydrogen-ion concentration for the medium in which they act. This variation is rapid at first, but then slackens and after a few years practically ceases. Thus a sample prepared in 1910 showed greatest activity in a medium slightly alkaline to phenolphthalein, but on keeping until 1914 it gave its maximum activity in a medium slightly acid to this indicator, and very little change was noticeable when it was further examined in 1920. W. G.

The Specific Action of the Urease of *Canavalia*. D. H. WESTER (*Rec. trav. chim.*, 1921, **40**, 320—322).—The urease obtained from *Canavalia* beans was specific in its action and did not decompose the substituted carbamides examined. W. G.

Action of Cyanogen Bromide on Triphenylphosphine. WILHELM STEINKOPF and KURT BUCHHEIM (*Ber.*, 1921, **54**, [*B*], 1024—1035).—It has been shown previously that tertiary arsines combine with cyanogen bromide in the complete absence of moisture to

form arsinebromocyanides which are hydrolysed to hydroxybromides with extraordinary readiness (this vol., i, 404, 471) but differ from the bromocyanides of tertiary amines in requiring a higher temperature for the elimination of alkyl bromide. The present communication deals with the intermediate phosphorus compounds, triphenylphosphine being used, since it is less readily autoxidisable than the trialkylphosphines.

Triphenylphosphine bromocyanide, $CN{\cdot}PPh_3Br$, is obtained as a snow-white, amorphous substance when molecular quantities of the components are mixed in the presence of perfectly dry light petroleum (the apparatus is described and figured in the original). It is extremely sensitive to moisture and the ratio, CN : P : Br, could only be determined in the product containing the solvent. The negative radicles are very readily replaced by the hydroxyl group (the cyanogen residue most readily as with the arsinebromocyanides), so that triphenylphosphine dihydroxide is ultimately obtained quantitatively. With an insufficient quantity of water partial hydrolysis takes place; but, whereas with the arsenic compounds the hydroxybromides only could be obtained, in the present instance a number of intermediate compounds could be isolated or identified, their formation depending on the mode of performing the reaction. When cyanogen bromide which has been distilled over calcium chloride (instead of over sodium as in the previous experiment) and triphenylphosphine are brought together in ether which has been dried in the usual manner, a mixture of varying proportions of soluble triethylphosphine oxide and insoluble *basic triphenylphosphine hydroxybromide*, $PPh_3(OH)_2,PPh_3Br{\cdot}OH$, is produced; the latter has m. p. 141·5°, and is the sole intermediate product which is stable towards air and non-hygroscopic. If the reaction is performed by distilling the cyanogen bromide directly over sodium into triethylphosphine dissolved in ether which has been dried as well as possible, it is occasionally possible to produce, although not to isolate, the bromocyanide; generally, however, *anhydrotriphenylphosphineoxybromide*, $O(PPh_3Br)_2$, m. p. about 140—150°, is obtained, the constitution of which is deduced from the observations that hydrocyanic acid is liberated during its formation and that it decomposes when heated in a vacuum with formation of triphenylphosphine and diphenylphosphinic acid,

$$PPh_3Br{\cdot}O{\cdot}PPh_3Br \longrightarrow PPh_3+C_6H_5Br+PPh{\cdot}OBr \longrightarrow PPh_2O{\cdot}OH.$$

When attempts are made to distil the ether in the above experiments in which triphenylphosphine bromocyanide is produced, the evolution of small amounts of hydrogen cyanide and considerable quantities of cyanogen is observed; the residue consists of *hexaphenyldiphosphonium bromide*, which, when heated further in a vacuum, passes into triphenylphosphine and its dibromide. The elimination of cyanogen is more easily observed when triphenylphosphine and cyanogen bromide are mixed in the absence of a solvent; the mixture becomes liquid and cyanogen is freely evolved; the action of water on the residue leads to the formation of viscous masses which do not contain triphenylphosphine oxide.

H. W.

Organic Compounds of Arsenic. III. The Action of Cyanogen Bromide on Phenyl*cyclo*pentamethylenearsine. WILHELM STEINKOPF and ARTUR WOLFRAM (*Ber.*, 1921, **54**, [*B*], 848—857).—The action of phenyl*cyclo*pentamethylenearsine (Grüttner and Wiernik, A., 1916, i, 92) on cyanogen bromide resembles that of triethylarsine. The primary additive product is hydrolysed with unusual ease, yielding *phenyl*cyclo*pentamethylene-arsine hydroxybromide*, $CH_2<\substack{CH_2\cdot CH_2\\CH_2\cdot CH_2}>AsPhBr\cdot OH$, small prisms, m. p. 162·5°, the constitution of which follows from its identity with the product derived from phenyl*cyclo*pentamethylenearsine dibromide. In the complete absence of moisture, however, it is possible to isolate *phenyl*cyclo*pentamethylenearsine bromocyanide*, as a voluminous, stable, crystalline substance, m. p. 107°. When heated somewhat above its melting point, it gives a yellowish-brown oil which is converted by bromine into cyanogen bromide and a liquid which yields its arsenic in ionised form when treated with alkali; the undissolved portion appears to consist of αε-dibromopropane. The course of the change is probably represented by the scheme: $C_5AsH_{10}PhBr\cdot CN \xrightarrow{Br_2} =C_5AsH_{10}PhBr_2+BrCN \rightarrow Br\cdot[CH_2]_5\cdot Br+AsPhBr_2 \xrightarrow{Br_2} AsPhBr_4 \rightarrow PhBr+AsBr_3$. If it is distilled under diminished pressure, a number of products are obtained which could not be separated completely by reason of the small amount of available material; phenyl*cyclo*pentamethylene-arsine is certainly regenerated and its dibromide is in all probability also produced. The cyano-group is eliminated as cyanogen and hydrogen cyanide, the latter being possibly due to inevitable, minimal traces of moisture. The absence of any evidence of ring fission is striking when compared with the behaviour of *N*-phenyl-piperidine. H. W.

Some Derivatives of Phenoxarsine. W. LEE LEWIS, C. D. LOWRY, and F. H. BERGEIM (*J. Amer. Chem. Soc.*, 1921, **43**, 890—896).—A comparison of diphenylchloroarsine with the three condensation products of arsenic chloride with diphenylamine, diphenyl ether, and phenyl-α-naphthylamine respectively shows marked differences in physical, chemical, and physiological properties. The first named, m. p. 37—38°, b. p. 333°, is irritant and toxic. 6-Chlorophenarsazine, m. p. 193°, is still more irritant and toxic, but 6-chlorophenoxarsine, m. p. 124°, and chlorophenyl-α-naphtharsazine, m. p. 228°, are less irritant to the skin and mucous membranes.

A number of derivatives have been prepared from 6-chlorophenoxarsine as follows. When dissolved in methyl alcohol and poured into a solution of potassium iodide in the same solvent, 6-chlorophenoxarsine yields 6-*iodophenoxarsine*, m. p. 144°. 6-*Bromophenoxarsine*, m. p. 128°, and 6-*thiocyanophenoxarsine*, m. p. 129°, are similarly prepared. By the addition of alkalis or sodium methoxide to an alcoholic solution of 6-chlorophenoxarsine, 6-*phenoxarsine oxide*, m. p. 182°, is obtained. 6-*Phenoxarsine sulphide*,

m. p. 161°, is prepared by passing hydrogen sulphide into an alcoholic solution of the chloro-compound. By the gradual addition of phosphorous acid to a boiling alcoholic solution of 6-phenoxarsine oxide, *phenoxycacodyl* (6 : 6-*bisphenoxarsine*), $O(C_6H_4)_2As{\cdot}As(C_6H_4)_2O$, m. p. 159°, is obtained. When 6-chlorophenoxarsine is oxidised by bromine in aqueous suspension or by hydrogen peroxide in glacial acetic acid, the product is *phenoxarsinic acid*, $O(C_6H_4)_2AsO{\cdot}OH$, m. p. 219°, giving a *sodium* salt. By Grignard's reaction, 6-chlorophenoxarsine may be converted into 6-*ethylphenoxarsine*, m. p. 218°, which gives a *diethylphenoxarsonium iodide*. W. G.

***cyclo*Hexane Compounds of Mercury.** MARC TIFFENEAU and E. GANNAGÉ (*Bull. Sci. Pharmacol.*, 1921, **28**, 7—14; from *Chem. Zentr.*, 1921, i, 766).—*cyclo*Hexane compounds of mercury are prepared by the action of sodium amalgam on bromine derivatives of *cyclo*hexane. *Mercury di*cyclo*hexyl*, $Hg(C_6H_{11})_2$, prepared by the action of sodium amalgam on *cyclo*hexyl bromide in ethyl acetate solution, forms white needles of a slight camphor-like odour, m. p. 139°, and can be sublimed in small quantities in a vacuum; with mercuric bromide or iodide it gives mercury bromo- and iodo-*cyclo*hexyl respectively. *Mercury* cyclo*hexyl chloride*, $C_6H_{11}{\cdot}HgCl$, prepared from mercury di*cyclo*hexyl and arsenic chloride or benzoyl chloride, crystallises in white needles, m. p. 159°, stable at ordinary temperatures; the *bromide*, $C_6H_{11}{\cdot}HgBr$, prepared by the action of sodium amalgam on *cyclo*hexyl bromide and mercury di*cyclo*hexyl, forms white spangles, m. p. 141°; the *iodide*, $C_6H_{11}{\cdot}HgI$, light yellow spangles, m. p. 142°; the *hydroxide*, $C_6H_{11}{\cdot}Hg{\cdot}OH$, is prepared from the haloids by the action of silver oxide; it is a strong base, decomposing on warming; the *cyanide*, $C_6H_{11}{\cdot}Hg{\cdot}CN$, prepared from the hydroxyl derivative, using 10% potassium cyanide solution, forms white spangles, m. p. 143°. *Mercury di*-4-*methyl*cyclo*hexyl*, $Hg(C_6H_{10}Me)_2$, a colourless liquid, D^{21} 1·459, cannot be distilled without decomposition. *Mercury* 4-*methyl*cyclo*hexyl chloride*, $C_6H_{10}Me{\cdot}HgCl$, forms spangles, subliming without melting at 163°; the *bromide* has m. p. 142°; the *iodide* has m. p. 176° (but also 66°); the *cyanide*, m. p. 100°; the *hydroxide*, $C_6H_{10}Me{\cdot}Hg{\cdot}OH$, forms spangles, m. p. 110° to 115°. G. W. R.

Organo-metallic Derivatives of Chromium, Tungsten, and Iron. GEORGE MACDONALD BENNETT and EUSTACE EBENEZER TURNER (*J. Roy. Soc. New South Wales*, 1919, **53**, 100—101).—Anhydrous chromic chloride reacts with magnesium aryl haloids to give compounds which, on decomposition with mineral acids, are quantitatively converted into the respective diaryl hydrocarbons (T., 1914, **105**, 1057). From experiments on the interaction of magnesium phenyl bromide and anhydrous ferric chloride it is concluded that, with both ferric and chromic chlorides, organo-metallic derivatives are formed. The chromium compound is at once decomposed by mineral acids, but the iron compound is more stable, the major portion remaining in the ethereal solution, from which it can be isolated as a green solid which is soluble in benzene

and depresses the melting point of diphenyl. With tungsten chlorides, Grignard reagents form unstable organo-metallic compounds which cannot be isolated. E. H. R.

Physiological Chemistry.

Blood as a Physico-chemical System. L. J. HENDERSON (*J. Biol. Chem.*, 1921, **46**, 411—419).—In the respiratory changes of blood, six simultaneous variables are involved, viz. the free and the combined oxygen of the whole blood, [O_2] and [HbO_2]; the free and combined carbonic acid of the serum, [H_2CO_3] and [$BHCO_3$]; the hydrogen-ion concentration of the serum, P_H, and its chloride concentration [BCl]. Any two of these six variables determine the whole equilibrium. The author describes the construction of a "nomogram," in which, by superposition of six systems of graphs, six co-ordinates may be read off for any given point, representing any given state of equilibrium of *defibrinated* blood. The nomogram thus represents the results for [$\overset{+}{H}$], [H_2CO_3] and [$BHCO_3$] (Henderson, A., 1908, ii, 467), as well as for [O_2], [HbO_2] and [H_2CO_3] (Barcroft, for instance, A., 1909, ii, 815) and for [H_2CO_3], [$BHCO_3$] and [HbO_2] (Christiansen, Douglas, and Haldane, A., 1914, i, 1012), and, in addition, it shows the relationships of the seventeen other combinations, in which the six variables can be taken, three at a time. The paper should have considerable didactic value. G. B.

Blood Sugar Regulation and the Origin of the Hyperglycæmias. I. Glycogen Formation and Glycogenolysis. II. Conditions of Action of Liver Diastases. III. Theory. EINAR LANGFELDT (*J. Biol. Chem.*, 1921, **46**, 381—390, 391—402, 403—409).—I. A review of the problem, from Bernard onwards; some of the later work leads to the supposition that glycogenolysis is favoured by acidity of the liver cells. II. In accordance with this, the author finds experimentally, *in vitro*, that the optimum for liver diastase in the presence of phosphate anions is at P_H 6·2, and with chlorine ions 6·8. When adrenaline is added, it is shifted to P_H 7·73. Thyroiodine alone has no influence, but in the presence of adrenaline (even 1 : 5,000,000) it causes increased glycogenolysis. III. The theory is illustrated by means of a diagram. The acidic optimum for liver diastase is a safety arrangement, securing a slow constant output of sugar and a fixed concentration of 0·09—0·1% in the blood. Part of the sugar is burnt, part stored in the muscles, the rest is recondensed to glycogen in the liver. The glycogen synthesis in the liver depends on the pancreatic hormone, and if the latter is inadequate, chronic hyperglycæmia and diabetes result. A different type of hyperglycæmia arises from increased breakdown

of glycogen in the liver owing to acidity or to a change in the optimum P_H (adrenaline). This type is transitory. G. B.

Relationship between Cholesterol and Cholesterol Esters in the Blood during their Absorption. ARTHUR KNUDSON (*J. Biol. Chem.*, 1921, **45**, 255—262).—A series of experiments on dogs shows that during the absorption of cholesterol and cholesterol esters the amount of cholesterol in the blood increases considerably, but that the amount of esters does not appreciably change. J. C. D.

Distribution of Carbon Dioxide between Cells and Plasma. L. W. SMITH, J. H. MEANS, and M. N. WOODWELL (*J. Biol. Chem.*, 1921, **45**, 245—253).—As the blood passes from the arterial to the venous side of the circulation in normal man its cells gain from 4—11 vol. % of carbon dioxide. At the same time, the corresponding gain in the plasma is only 0 to 1·8 vol. %. It is concluded that the carbon dioxide is transported mainly by the cells. J. C. D.

Permeability of the Red Corpuscles for Amino-acids. SHUZO KOZAWA and NOBU MIYAMOTO (*Biochem. J.*, 1921, **15**, 167—170).—On the addition of isotonic solutions of glycine and histidine to whole blood, the amino-acid nitrogen of the corpuscles (estimated by van Slyke's method) shows a large increase.

This result was obtained with the blood of the ox, goat, and man, and confirms the result previously found by Costantino (A., 1913, i, 1259) for ox blood. C. R. H.

Nephelometric Estimation of Quinine in Blood. HUGH WILLIAM ACTON and HAROLD KING (*Biochem. J.*, 1921, **15**, 53—59).—The method of Ramsden and Lipkin (A., 1918, ii, 251; 1919, i, 106) is criticised. It is impossible to recover the whole of quinine from blood, but with elaborate care as regards manipulation and purity of reagents a fairly constant proportion (70—80%) may be recovered and estimated. In this way it is found that serum contains about as much quinine as an equal volume of corpuscles, in opposition to the conclusion of Morgenroth, that it is preferentially fixed on the corpuscles; hence the latter's theory of the action of quinine in malaria is unfounded. One hour after taking 1 gram of quinine by the mouth, the blood of one of the authors contained 33 mg., or 3·3%, of the dose taken. This is a concentration of 1 in 150,000 or 20 millions of quinine molecules per blood corpuscle. In the following hours the concentration fell somewhat. G. B.

Calcium Metabolism. W. P. WHEELER (*New York Agric. Expt. Sta.*, Bull. 468, 1919).—Experiments with common fowls and ducks showed that magnesium does not replace calcium in the bones from which it is withdrawn for shell material, but when strontium salts are fed with rations of low calcium content, strontium replaces calcium in the bones of the mature birds. W. P. S.

Enzyme Formation [in the Organism]. H. Staub (*Helv. Chim. Acta,* 1921, **4**, 281—287).—In order to obtain information regarding carbohydrate metabolism, the author makes use of the "blood sugar curve," obtained by determining the percentages of sugar in the blood at frequent intervals and plotting the results as ordinates against times as abscissæ. It is found that ingestion of carbohydrate is followed by enhanced assimilation of dextrose, whereas, if carbohydrate food is stopped for some time, the capacity for assimilating dextrose is depressed. These results, which are regarded as due to sufficiency or lack of what are named "assimilation enzymes," are discussed in their relation to the formation of enzymes in the human organism. T. H. P.

Comparative Metabolism of Proteins of Unlike Composition. Walter G. Karr [with Edward Tolstoi] (*J. Biol. Chem.*, 1921, **45**, 289—295).—As far as is indicated by the urinary nitrogenous end-products, the metabolism of two proteins, caseinogen and wheat gluten, widely different in their chemical composition, is essentially the same. In experiment with yeast as a sole source of protein 80% of the nitrogen was assimilated, but no abnormality of the partition of urinary nitrogen was observed. J. C. D.

Effects of Heat and Aeration on Vitamin-*A*. Frederick Gowland Hopkins (*Biochem. J.*, 1920, **14**, 725—733).—No appreciable difference was observed in the amount of vitamin-*A* in samples of ground-nut oil and palm kernel oil before and after the usual refining processes. The amount present in all cases was very small. The vitamin-*A* displays marked resistance to heat alone at temperatures up to 120°, but is readily destroyed when heated with simultaneous aeration. This vitamin appears to be a substance prone to oxidation with resulting inactivation. J. C. D.

Vitamin-*A*. VI. Effect of Heat and Oxygen on the Nutritive Value of Butter. Jack Cecil Drummond and Katharine Hope Coward (*Biochem. J.*, 1920, **14**, 734—739).—Destruction of vitamin-*A* in butter occurs on heating in the presence of air. It is therefore probable that the loss is due to changes of an oxidative nature. The destruction is rapid at high temperatures, but may also occur with readiness at temperatures as low as 37°, if contact with air or oxygen is extensive (see preceding abstract). J. C. D.

The Action of Ozone on Vitamin-*A* in Fats. Sylvester Solomon Zilva (*Biochem. J.*, 1920, **14**, 740—741).—Exposure of butter or cod-liver oil to ozone rapidly destroys the vitamin present. This confirms the destruction by air or oxygen reported by Hopkins and Drummond and Coward (see preceding abstracts). J. C. D.

Accessory Food Factors. I. Special Nutrition Values of Different Fats. Hans Aron and Richard Gralka (*Biochem. Zeitsch.*, 1921, **115**, 188—203).—Feeding experiments on rats are described which confirm the presence of vitamin-*A* in cod-liver oil, butter, and egg-yolk and its absence in margarine. E. S.

Dielectric Constants of Biochemical Substances. RUDOLF KELLER (*Biochem. Zeitsch.*, 1921, **115**, 134—158).—A vigorous criticism of the too extensive application of the ionic theory to biology and colloid chemistry. Statical electricity has been neglected, although it is quite as important to biology as galvanic. Almost all technical insulators are of animal or vegetable origin and more attention should be paid to the dielectric constant of biologically important substances. The dependence of the sign of the electric charge on the dielectric constant of substance and medium, discovered by Coehn, is of prime importance to biology. Protein molecules and others of similar size scarcely ever react chemically, but chiefly form compounds through their electrostatic surface charge. The only experimental material contained in this paper is a table of the dielectric constants of eighteen substances. G. B.

Lecithin. IV. Lecithin of the Brain. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1921, **46**, 353—365).—The ethereal extract of 200 ox brains yielded 400 grams of crude lecithin; part of the cerebrosides was precipitated by dissolving the sample in glacial acetic acid, and addition of 10 volumes of 95% alcohol threw down kephalin from the filtrate. The final separation from kephalin is effected with cadmium chloride, and on reduction crystalline hydrolecithin is obtained. A pure product is more easily got from the acetone extract of brain.

The lecithin of brain seems to be very similar to that of egg yolk (this vol., i, 382) and contains palmitic, stearic, and oleic acids. G. B.

Pentose Mononucleotides of the Pancreas of the Dogfish (*Squalus Sucklii*). C. BERKELEY (*J. Biol. Chem.*, 1921, **45**, 263—275).—The β-nucleoprotein of the pancreas of the dogfish contains both adenine and guanine in pentose mononucleotide combination. This β-nucleoprotein is readily broken down to its constituent mononucleotides and protein by the action of cold 1% sodium hydroxide.

The mononucleotides thus obtained are not precipitated from either neutral or acetic acid solution. The guanine mononucleotide differs in this respect from the guanylic acid previously isolated from mammalian material. J. C. D.

Rigor Mortis in Smooth Muscle and a Chemical Analysis of Fibromyoma Tissue. EDWIN F. HIRSCH (*J. Biol. Chem.*, 1921, **45**, 297—306).—The post-operative rigor of smooth muscle is manifested by changes similar to those known in skeletal muscle as rigor mortis. The increase in acidity is accompanied by a decrease in reducing carbohydrates and of alkaline reserve. A chemical analysis of fibromyoma tissue is given. J. C. D.

Bromine Normally Present in Animal Tissues. A. DAMIENS (*Bull. Soc. Chim. Biol.*, 1921, **3**, 95—104).—The estimations were made by Denigès's colorimetric method (A., 1912, ii, 1208). A scheme for the separation and estimation of chlorine, bromine, and

iodine is given. All normal organs contain bromine; the amount in the human lung is about 0·30 mg. per 100 grams. That of chlorine is about 260 mg. and the ratio Br : Cl=0·00140 obtained does not vary greatly in a large number of other human and animal organs. In dogs poisoned with benzyl bromide, bromoacetone, etc., the amount in the organs rises to 1 or even 2 mg. per 100 grams as compared with 0·40 mg. normally present, and the method has been applied in human toxicology to ascertain whether death was due to a brominated substance. In such cases the highest Br : Cl ratio observed was 0·00386. G. B.

Constituents of the Japanese Common Earth-worm. YOSHIHARU MURAYAMA and SHINJIRÔ AOYAMA (*J. Pharm. Soc. Japan*, 1921, 221—240).—Dried earth-worm (*Lumbricus spenceri*), now used as an antipyretic in Japan, was finely powdered and extracted with cold ether. The syrup (2·3%) left on evaporation contained free acids, esters, and 31·2% of unsaponifiable matter. The acids, both free and as esters, were stearic and palmitic acids, together with a mixture of highly unsaturated fatty acids, from which bromine compounds containing 62·67%, 63·7%, and 65·13% of bromine were prepared. The unsaponifiable matter on hydrolysis with alcoholic potassium hydroxide yielded cholesterol. The residue contained a lipoid (P 3·96%), and a mixture of amino-acids, from which leucine and valine were isolated. From another sample tyrosine was isolated, and its presence was also proved in the warm water extract from the fresh earth-worm. K. K.

Vitamin Content of Milk. FREDERICK GOWLAND HOPKINS (*Biochem. J.*, 1920, **14**, 721—724).—Confirmation is given of the author's original observations regarding the minute supplement of milk necessary to make good the vitamin deficiency of an artificial diet of pure proteins, carbohydrates, fats, and salts (*J. Physiol.*, 1912, **44**, 425). The possibility of there being a seasonal variation in the vitamin content of milk, or of the growth energy of the test animals must be borne in mind. J. C. D.

Presence in Urine of Nitrogen Not Determined by the Kjeldahl Method. W. MESTREZAT and (MLLE) MARTHE PAUL JANET (*Bull. Soc. Chim. Biol.*, 1921, **3**, 88—94).—The Dumas method indicates a somewhat larger amount than the Kjeldahl-Foerster method (6·2—9·7% in the urine after purgation, 1·5—4·9% in more normal urines). This may be due to the presence of pyridine or pyrazole nuclei (compare Dakin and Dudley, A., 1914, ii, 381). G. B.

A Human Enterolith containing Choleic Acid. HENRY STANLEY RAPER (*Biochem. J.*, 1921, **15**, 49—52).—A "stone" from the jejunum, removed in a case of intestinal obstruction, weighed 6·8 grams and contained fatty acids 10·85%, neutral fat and unsaponifiable substances 5·52%, unconjugated bile acids (almost wholly choleic acid) 72·5%, food residues 8·4%, ash 1·19%. G. B.

Glyoxalase in Avian Beriberi. GEORGE MARSHALL FINDLAY (*Biochem. J.*, 1921, **15**, 104—106).—Confirmation of the results of Dutcher (A., 1918, i, 561) that the glyoxalase content of the liver in pigeons with beriberi is less than that in control pigeons, or in pigeons cured by administration of vitamin-*B*. The vitamin does not act as a co-enzyme of glyoxalase. G. B.

Narcotic Action of Light Petroleum (Pentane, Hexane, Heptane, Octane). HERMANN FÜHNER (*Biochem. Zeitsch.*, 1921, **115**, 235—261).—In contradistinction to ether and chloroform, the above hydrocarbons when inhaled (by mice and rats) often cause great excitement and they soon affect the respiration adversely; benzene is an even more powerful excitant. In equimolecular concentration, benzene is a somewhat less powerful anæsthetic than chloroform; ether has only one-quarter of its activity. Hexane and ether are about equally powerful; so are heptane and benzene, octane and chloroform. In the series pentane to octane each member is about three times as active as its lower homologue and is about one-third as soluble in water. G. B.

Physiological Action of Oxalates, Citrates, and Tartrates. SHOHEI HARA (*Acta Schol. Med. Univ. Imperial Kioto*, 1919, **3**, 213—232. See also A., 1910, ii, 434; A., 1911, ii, 1016; A., 1914, i, 1189).—The sodium salts of oxalic, citric, and tartaric acids exert a specific action in addition to their precipitation of calcium, since their toxicity is not in the ratio of their ability to precipitate calcium salts. Neither is the detoxicating action of calcium chloride measurable by the solubility of the calcium salts formed. The power of these acids to intensify the action of magnesium corresponds with their power to precipitate calcium, and is probably due to a change produced by them in the equilibrium between the ions of calcium and those of magnesium.

CHEMICAL ABSTRACTS.

The Behaviour of Formaldehyde in the Animal Body. E. SALKOWSKI (*Biochem. Zeitsch.*, 1921, **115**, 159—167).—Experiments described show that the rapid disappearance of formaldehyde from the blood after intravenous injection is due neither to combination with blood-proteins nor to the action of alkali in the blood. It is therefore concluded that it is absorbed by the organs, in the cells of which it is slowly oxidised.

Incidentally it is shown that formaldehyde will not distil from aqueous solutions containing 1% of sodium carbonate, but it passes over on acidification. Further, by boiling aqueous formaldehyde solutions containing 0·5% or 0·25% of sodium carbonate for two hours, a portion is converted into formose. E. S.

Natural Immunity of the Rabbit to Atropine. H. C. VAN DER HEYDE (*Arch. Néerl. physiol.*, 1921, **5**, 380—433).—Atropine is first bound physically by the serum of rabbits, cats, etc., is then rendered physiologically inert, and destroyed chemically. Organ press juices of the rabbit destroy atropine much more rapidly than

do those of the cat; on this the natural (cellular) immunity of the rabbit seems to depend. The substance destroying atropine is probably formed by the leucocytes. The method of analysis employed was precipitation by Mayer's reagent. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Uranium Salts on a Nitrogen-fixing Organism. E. KAYSER (*Compt. rend.*, 1921, **172**, 1133—1134).—The influence of uranium salts on *Azotobacter agile* depends on the nature of the salt used, its concentration, and the colour of the containing vessel. Uranium acetate gave an increased fixation of nitrogen and better utilisation of either mannitol or dextrose with cultures in colourless glass, but not in yellow glass, but uranium phosphate showed a diminution in fixation and poorer utilisation of mannitol with cultures either in colourless or yellow glass. W. G.

Microchemistry of Micro-organisms. I. Biochemistry of *Bacillus mesentericus vulgatus*. W. GRIMMER and B. WIEMANN (*Forsch. Geb. Milchwirt.*, 1921, **1**, 2—18; from *Chem. Zentr.*, 1921, i, 775).—*Bacillus mesentericus vulgatus* contains a proteolytic enzyme which in a very weak acid medium hydrolyses casein to its simplest constituents. The following products were identified: alanine, valine, leucine, tyrosine, aspartic acid, glutamic acid, proline, arginine, lysine, histidine, tryptophan, and perhaps phenylalanine. In the presence of lactose, proteolysis is not so complete and the following products were identified: putrescine, cadaverine, tryptamine, tyrosol, and ammonia. G. W. R.

The Cycloclastic Power of Bacteria. II. A Quantitative Study of the Aerobic Decomposition of Tryptophan and Tyrosine by Bacteria. HAROLD RAISTRICK and ANNE BARBARA CLARK (*Biochem. J.*, 1921, **15**, 76—82).—The previous work of Raistrick (A., 1920, i, 348) on the bacterial decomposition of histidine is extended to tryptophan and tyrosine. Experiments were conducted both in the presence and absence of glycerol, and the fate of the amino-acids was followed by estimation of the distribution of the nitrogen in the medium, with the addition (in the case of tyrosine) of estimation of phenolic groups.

The indole nucleus of tryptophan is ruptured by all organisms tried except *B. proteus vulgaris*; in all cases the phenolic group of tyrosine disappears, but the question of the rupture of the benzene nucleus is left open.

In all cases the addition of glycerol is accompanied by a small formation of ammonia and a large proportion of synthesised nitrogen; the reverse is found in the absence of glycerol. In view of this

observation an explanation is suggested of the so-called "protein-sparing" action of carbohydrates. C. R. H.

The Cultivation of Yeast in Solutions of Purified Nutrients. MARGARET B. MACDONALD and E. V. MCCOLLUM (*J. Biol. Chem.*, 1921, **45**, 307—311).—Yeast has been grown in nutrient solutions containing no possible source of the vitamin-*B* to such an extent as to make the authors question whether this substance is necessary for the growth of the organism. If it is necessary the yeast synthesises its own supplies. J. C. D.

Carboligase: A Ferment Linking Carbon Chains. CARL NEUBERG and JULIUS HIRSCH (*Biochem. Zeitsch.*, 1921, **115**, 282—310).—A re-investigation of the phytochemical reduction of benzaldehyde by yeast (A., 1914, i, 785) in the light of the recent theory of alcoholic fermentation (A., 1920, i, 124) showed that in addition to benzyl alcohol a hydroxy-ketone of the constitution OH·CHMe·COPh or OH·CHPh·COMe (the former being regarded as the more probable) was formed. The free compound was obtained in a crude state, but could not be purified. It was characterised by means of the semicarbazone, thiosemicarbazone, and *p*-nitrophenylosazone, which were identical with the compounds obtained by v. Auwers (A., 1918, i, 18) from α-bromopropiophenone. The *phenylhydrazone*, m. p. 96°, was also prepared as well as a crystalline bisulphite compound.

The compound is formed during the fermentation of sucrose or dextrose by either top-yeast or bottom-yeast in the presence of benzaldehyde. Maceration juice is equally effective, but the product in this case is optically inactive, that obtained by using living yeast being lævorotatory.

The reaction is regarded as being a condensation of the benzoin type between one molecule each of benzaldehyde and acetaldehyde, the latter being produced as an intermediate product of fermentation. Further, the effective substitution of maceration juice for the living yeast indicates that the condensation is produced under the influence of an enzyme contained in yeast. To this enzyme the name *Carboligase* is given. It is the first example of an enzyme which links together carbon atoms.

Attempts to bring about the direct condensation of the two aldehydes by the action of yeast were unsuccessful, but by replacing the acetaldehyde by pyruvic acid, its parent in alcoholic fermentation, the above hydroxy-ketone was again produced. Hence it follows that, unless the nascent acetaldehyde produced by decarboxylation of pyruvic acid is specially active, it is the latter substance which condenses with the benzaldehyde, the resulting compound being subsequently decarboxylated. E. S.

Effect of Acetaldehyde and Methylene-blue on the Fermentation of Dextrose and Lævulose by Yeast-juice and Zymin in Presence of Phosphate and Arsenate. ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1921, **15**, 175—185).—An extension to lævulose of previous work on dextrose (A., 1920,

i, 914). Acetaldehyde diminishes the time required by a lævulose and phosphate mixture to attain its maximum rate of fermentation in the presence of yeast-juice or zymin, but the maximum rate obtainable is not substantially increased. In the presence of acetaldehyde, lævulose is fermented more rapidly than dextrose. Acetaldehyde is fifty times as effective as lævulose in accelerating the fermentation of a dextrose–phosphate mixture. Methylene-blue behaves like acetaldehyde. Arsenate does not affect the acceleration by acetaldehyde in the presence of phosphate and yeast-juice, but causes a considerable acceleration with zymin, particularly in the case of dextrose. G. B.

Researches on Fermentation. VII. The Influence of Additions (Toluene, Chloroform, Thymol, and also of Neutral Salts) on the Fermentative Decomposition of Dipeptides by Yeast Extract. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1920—1, **4**, 191—208).—Experiments were carried out on the fermentation of glycyl-*l*-leucine by yeast extract, the course of the reaction being followed at intervals of ten minutes by the formaldehyde titration method. The addition of toluene, chloroform, and thymol had no effect on the fermentation, which is explained by the fact that these compounds have no influence on the colloid state of the yeast enzymes. The addition of small amounts of sodium chloride caused a little retardation in the reaction, which was increased by increasing the amount of salt added. Whether the yeast extract were fresh or old made little material difference. With additions of potassium chloride, bromide, nitrate, and sulphate, there was a slight acceleration of the reaction during the first time interval, followed by a slight retardation and then a rapid stopping. This result was given by a concentration of a two-thirds equivalent of each salt per litre; with higher concentrations, the stopping came at an earlier stage. Potassium iodide and thiocyanate produced at once a great diminution in the reaction. The influence of the salt added is of a complex nature and depends on the change produced in the electric charge of the solution and on the change of state of the colloids produced thereby. The addition of the neutral salt has the effect of displacing the hydrogen-ion concentration towards the acid side. J. H. J.

Influence of Sodium Chloride on the Development of *Sterigmatocystis nigra* (*Aspergillus niger*). MARIN MOLLIARD (*Compt. rend.*, 1921, **172**, 1118—1120).—At a concentration of 0·25—0·75%, sodium chloride has practically no effect on the rate of development of *Aspergillus niger*, but at concentrations above this the velocity of development, the total weight of mycelium, and the ratio of mycelium produced to sugar utilised diminish as the concentration of the sodium chloride increases, until at a concentration of 12% development ceases. Further, with concentrations of sodium chloride above 3% there is no formation of conidia, but this action is secondary and due to the accumulation of nitric acid from the ammonium nitrate. W. G.

Effect of Zinc and Iron compared with that of Uranium and Cobalt on the Growth of *Aspergillus*. R. A. STEINBERG (*Bot. Gaz.*, 1920, **70**, 465—468).—The observation of Raulin (*Ann. Sci. nat. bot.*, 1869, [v], **11**, 93) and of Javillier (Thesis, Paris, 1908; see also A., 1908, ii, 124 and 317) that iron and zinc are essential for the growth of *Aspergillus niger* is confirmed. (Further, see A., 1911, ii, 421, 644; A., 1912, ii, 192, 377, 861; A., 1913, i, 686, 692, 1423; A., 1914, i, 238, 239, 787; A., 1916, i, 237; A., 1920, i, 267.) CHEMICAL ABSTRACTS.

Enzyme Formation by *Penicillium glaucum*. H. VON EULER (*Fermentforsch.*, 1920—1, **4**, 242—257).—Experiments were made on the inversion of different sugar solutions by *Penicillium glaucum*. The conditions of the experiments as to percentage of sugar, age, and state of fructification of the fungus, and temperature were varied. The saccharase content of the fungus as evidenced by the inversion produced was calculated from the formula, Inversion Capacity = Inversion Constant × weight of sugar/weight of dry substance of fungus. It was found that the inversion capacity was highest on the fourth day of growth and at a temperature under 16°. The conidia of the fungus had only a third of the inversion capacity of the mycelium. The highest inversion capacity was exhibited in solutions of cane-sugar and galactose. The general conclusion was that *Penicillium glaucum* contains but a tenth of the saccharase content of bottom yeast and a sixth of that of top yeast. J. H. J.

Nitrogenous Metabolism of the Higher Plants. I. Isolation of Proteins from Leaves. ALBERT CHARLES CHIBNALL and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1921, **15**, 60—75).—Green leaves are extracted with water saturated with ether; on warming the opalescent solution to 40°, a colloidal precipitate containing 10% N is deposited consisting of crude protein; methods of partial purification are described. G. B.

Relation of Potassium to the Growth of Plants. T. O. SMITH and O. BUTLER (*Ann. of Bot.*, 1921, **138**, 189—225).—The authors have studied the relation of potassium to plant growth, using buckwheat, wheat, and maize. Growth was investigated both in water and in sand cultures, using nutritive solutions with and without potassium salts.

The reserve supply of potassium in the seed is insufficient to maintain normal growth beyond a short period. The symptoms of potash starvation are dwarfing of the axis and progressive death of the foliage. The absorption of potassium relative to the amount of dry matter formed is greater in normally nourished plants than in plants suffering from potassium starvation. The relation between the potassium contents of the dry matter of tops and roots is unaffected by the presence or absence of potassium in the nutritive medium.

When potassium is added to plants growing without this element,

recovery occurs the more slowly the longer it is withheld. There is no evidence for a specific effect of potassium on carbohydrate synthesis and translocation. G. W. R.

Influence of certain Organic Compounds on the Development of Plants. V. G. CIAMICIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 3—7. Compare A., 1920, i, 408).—Although to a less extent than *iso*amylamine, butylamine causes albinism in the leaves of plants. Experiments made with quinoline and tetrahydroquinoline, phthalic and tetrahydrophthalic acids, and cymene and limonene show that in each case the hydrogenated compound is the more toxic. α-Naphthylamine is more poisonous than aniline, and also quinoline and *iso*quinoline more so than pyridine; hence, bases with condensed nuclei appear to be more highly toxic than those with simple nuclei. The influence of the length of the carbon-atom chain (*loc. cit.*) is not confirmed by the results of experiments with formic, acetic, propionic, butyric, valeric, *iso*-valeric, hexoic, lauric, and palmitic acids.

Investigation of the resistance to oxidation by bean and maize plants and by pulped spinach leaves exhibited by catechol and guaiacol, morphine and codeine, theobromine and caffeine, and atropine and cocaine shows that the substances which are the more injurious to plants are those which are the better able to withstand enzymic oxidation. The bearing of this result on the problem of the function of alkaloids in plants is discussed. Plants need as stimuli certain alkaloids and utilise products of their metabolism, such as xanthine, but, in order to render these products resistant to oxidation or other eliminating agencies, the plants convert them into more stable compounds by the introduction into their molecules of alkyl or acid radicles. Side-chains may, however, fulfil other functions, since they do not in all cases cause increased resistance to oxidation.

That only plants containing a given poison are immune to the latter is confirmed by the behaviour of eserine, which is present in *Physostigma venenosum*, but is highly toxic to the ordinary bean and to tomato plants.

Unlike pyrogallol, tannin exerts no poisonous action on various plants examined, this result being in agreement with those obtained with glucosides and in disagreement with the view of Bernardini (*Rend. Soc. Chim. Ital.*, 1913, **5**, 278). The action of tannin appears to be limited to the production of a deficient development, the resulting plants being small but well proportioned. T. H. P.

The Osmotic Concentration and Electrical Conductivity of the Tissue Fluids of Ligneous and Herbaceous Plants. J. ARTHUR HARRIS, ROSS AIKEN GORTNER, and JOHN V. LAWRENCE (*J. Physical Chem.*, 1921, **25**, 122—146).—Studies in the Arizona deserts, in the Jamaican montane rain forest, and in the mesophytic habitats of the north shore of Long Island, have shown that the osmotic concentration as measured by the cryoscopic method is far higher in the leaf-tissue fluids of ligneous than of herbaceous

species, whilst in the case of determinations made in the various non-halophytic habitats of the north shore of Long Island the electrical conductivity was lower for the expressed juice of leaf-tissues of ligneous species than for that of herbaceous forms. The concentration of ionised solutes is lower in ligneous than in herbaceous forms, whilst the reverse is true of total solutes. This is believed to be a general law. J. R. P.

Formation of Hydrocyanic Acid in Plants. PAUL MENAUL (*J. Biol. Chem.*, 1921, **46**, 297).—The formation of hydrocyanic acid was observed *in vitro* in sunlight, in a solution containing potassium nitrate and formaldehyde, but only if the reaction was acid to methyl-orange. It is suggested that hydrocyanic acid may thus be formed in plants. G. B.

The Hydrocyanic Acid Question. V. Treub's Hypothesis. L. ROSENTHALER (*Schweiz. Apoth.-Zeit.*, 1920, **58**, 137—142; from *Chem. Zentr.*, 1921, i, 773—774).—A theoretical discussion of the part played by hydrocyanic acid in the process of nitrogen assimilation. The facts hitherto established are insufficient to prove or disprove the hypothesis that hydrocyanic acid is the first recognisable product of nitrogen assimilation and it is probable that the rôle of this compound is not the same in all cases. G. W. R.

The Hydrocyanic Acid Question. VI. Hydrocyanic Acid Content of the Leaves of Cherry Laurel. L. ROSENTHALER (*Schweiz. Apoth.-Zeit.*, 1921, **59**, 10—13, 22—26; from *Chem. Zentr.*, 1921, i, 774).—At the period when the leaves are developing, the youngest leaves show the highest content of hydrocyanic acid. In the later stages of growth the distinction is not so marked. The distribution in individual leaves is uniform as a rule, except that, particularly in young leaves, the mid-rib is richer in hydrocyanic acid than the rest of the leaf. G. W. R.

Variation of Organic Acids in the Course of Anthocyanic Pigmentation. (MLLE) DENISE KOHLER (*Compt. rend.*, 1921, **172**, 709—711).—The results of analyses on organs attached to the plant appear to be contradictory, but in organs detached from the plant there is no apparent correlation between the formation of anthocyanin and the content of organic acids in the organs. W. G.

Differentiation of the Yellow Plant Pigments from Vitamin-*A*. MARJORY STEPHENSON (*Biochem. Journ.*, 1920, **14**, 715—720).—The vitamin-*A* present in carrots may be prepared in the form of an extract made with alcohol and light petroleum. The observation of Drummond (A., 1919, i, 362) that carrotin is not identical with vitamin-*A* is confirmed.

The pigment of butter fat may be removed or destroyed by filtration through charcoal without apparently affecting the vitamin content. J. C. D.

Anthocyanins and Anthocyanidins. IV. Observations on: (*a*) Anthocyanin Colours in Flowers, and (*b*) the Formation of Anthocyanins in Plants. ARTHUR ERNEST EVEREST and ARCHIBALD JOHN HALL (*Proc. Roy. Soc.*, 1921, [*B*], **92**, 150—162; compare Willstätter and Everest, A., 1913, i, 1371; Willstätter and Mallison, 1915, i, 282, 289).—For the most part a reply to Shibata, Shibata, and Kasiwagi (A., 1919, i, 166) and a criticism of their work. The blue colour of flowers containing anthocyanin may be due to the presence of either (1) anthocyanin phenoxides of alkali or alkaline-earth metals; or (2) complex anthocyanin-iron salts.

Further experiments are described in support of the view that, in nature, the anthocyanin colouring matters are produced by reduction from yellow sap pigments of the flavonol group (compare A., 1915, i, 25; 1918, i, 420). W. G.

Oxydases. The Bach-Chodat System. OBDULIO FERNÁNDEZ (*Ann. Fís. Quím.*, 1921, **19**, 109—114).—A discussion, mainly theoretical, of the action of peroxydases in plants. It is shown that the juices of certain plants which contain an incomplete peroxydase system can produce the blue colour with guaiacum in the presence of oxybrucine or oxystrychnine. G. W. R.

Oxidising Enzymes. IV. Distribution among the Higher Plants. V. Further Observations on the Oxidising Enzymes of Fruits. MURIEL WHELDALE ONSLOW (*Biochem. J.*, 1921, **15**, 107—112, 113—117).—I. Three-fifths of the orders of Angiosperms were examined and 62% contain species with an oxydase. II. Continuation on the lines of previous work (A., 1920, i, 920); examination of a further sixteen common fruits. G. B.

Action of some Alkaloids on *Botrytis cinerea*, Pers. PIERRE NOBÉCOURT (*Compt. rend.*, 1921, **172**, 706—708).—Nicotine and atropine do not appear to be injurious to the growth of *Botrytis cinerea*, Pers., on Raulin's liquid, even at concentrations higher than those ever attained in the tissues of tobacco or belladonna plants. Quinine exerts an unfavourable influence only at concentrations of the order of 2%. On the other hand, aconitine is decidedly injurious even at low concentrations. W. G.

The Anthocyanins of *Beta vulgaris*, L., and *Raphanus sativus*, L. GUSTAV SCHUDEL (*Diss.*, *Zürich*, 1918, 1—64. See A., 1920, i, 515).—For the separation of diglucosides, monoglucosides, and anthocyanidins in the same solution, a table of solubilities is given, and a method for the detection and estimation of these substances is described. Anthocyanins are obtained in a pure state by way of their chloro- or dichloro-picrates; the preparation of chloro- and dichloro-picric acid is also described. From red beets the colouring matter *betanin* is separated as a bronze-green, lustrous powder, having the properties of a glucoside, and containing 55·16% C, 4·96% H, and 8·57% N. Elimination of sugar yields *betanidin*; on account of its instability this substance was obtained

only as *ethylbetanidin*, a violet-red substance containing 60·24% C, 5·27% H, and giving a qualitative test for nitrogen. Solutions in methyl and ethyl alcohols are more stable than those in dilute hydrochloric acid or water; stability is greatest in hydrogen chloride-absolute alcohol solution protected from water, but on long keeping the solutions become colourless. From the peelings of yellowish-red radishes, *raphanin hydrochloride* is obtained as a lustrous vermilion powder containing 52·49% C, 5·28% H, and 5·63% Cl. Raphanin is a diglucoside, easily soluble in methyl alcohol, in water, and in hydrogen chloride-absolute alcohol if warm. Solutions eventually become decolorised owing to isomerisation. The corresponding anthocyanidin, *raphanidin*, is identical with pelargonidin. Violet radishes yielded the pigment *rubin*, a dark carmine-red diglucoside, soluble in hydrochloric acid and in methyl alcohol, but sparingly soluble in ethyl alcohol. *Rubidin* is identical with cyanidin. CHEMICAL ABSTRACTS.

Distribution of Nitrogen in Lucerne Seed. HARRY G. MILLER (*J. Amer. Chem. Soc.*, 1921, **43**, 906—913).—When lucerne seed was ground and extracted with 0·5% aqueous potassium hydroxide and the extract poured into its own volume of alcohol, the carbohydrate material separated out as a slime and the supernatant liquid could be easily filtered. The protein precipitated from the filtrate by acid represented 60% of the total nitrogen in the seed. It contained histidine, arginine, lysine, and cystine, and gave the test for tryptophan. The free amino-nitrogen of the protein corresponded with nearly one-half of the lysine nitrogen found. The nitrogen distribution in the seed was determined by van Slyke's method and by precipitating different fractions in the alkali extract of the seed. W. G.

Seeds of the Papilionaceæ Family with Hydrosulphide Autofermentation. MARCEL MIRANDE (*Compt. rend.*, 1921, **172,** 1202—1204. Compare *ibid.*, 1921, **172,** 1142).—Numerous seeds when crushed and moistened with a little water have been found to undergo autofermentation with the liberation of hydrogen sulphide. Such are *Lathyrus odoratus*, all the kidney beans; *Phaseolus vulgaris*; the peas; the beans, *Faba vulgaris* and its varieties; different species of *Vicea*; the chick-pea, *Cicer arietinum*; and lucerne. In all these cases there is active evolution of hydrogen sulphide, and in other species the action can be observed but is less vigorous. W. G.

Microchemical Examination of certain Orchids for Alkaloids and Tannin. D. H. WESTER (*Ber. deut. Pharm. Ges.*, 1921, **31**, 179—183).—A microchemical examination was made of various organs of thirty-three orchidaceous plants cultivated in the Netherlands. In no case could tannin be detected, and in only three instances were alkaloids found. In the case of *Phalænopsis amabilis* the quantity of alkaloid present was sufficient to allow of its isolation, but the composition and properties could not be

determined. None of the plants investigated yielded hydrocyanic acid. G. F. M.

The Acid Constituents of the Gem of the Pine: *d*- and *l*-Pimaric Acids. GEORGES DUPONT (*Compt. rend.*, 1921, **172**, 923—925).—By the use of aqueous alcohol as a solvent the author has been able to isolate appreciable quantities of *l*-pimaric acid from the resin of the leaf buds of *Pinus maritima*. The ready preparation of *d*-pimaric acid from this source is due to the fact that the lævo-acid accompanying it usually undergoes isomerisation during the acid treatment commonly used for its isolation.
W. G.

The Sugar of the Fruit of *Phytolacca dioica*, Linn. VICTOR ARREGUINE (*Anal. Soc. Quím. Argentina*, 1920, **8**, 229—232).—The fruit of *Phytolacca dioica*, Linn. (Ombù), has been shown to contain 11·2% of non-reducing sugar (Balland, A., 1881, 1151). The author has isolated this sugar in a crystalline state. The aqueous solution does not reduce Fehling's solution, but reduces readily after hydrolysis with dilute mineral acid. The original solution is optically active, $[\alpha]_D^{20} + 76·9°$. The hydrolysed solution gives $[\alpha]_D^{5} - 26·9°$. Pentoses and mannose were shown to be absent. Oxidation with nitric acid gave saccharic acid. The osazone obtained from the hydrolysed solution was identical with glucosazone. It is concluded, therefore, that the sugar in question is sucrose. G. W. R.

The Active Constituents of Shepherd's Purse (*Capsella bursa pastoris*). H. BORUTTAU and H. CAPPENBERG (*Arch. Pharm.*, 1921, **259**, 33—52).—Physiological investigation showed the extracts of the drug to contain a very marked depressor substance subsequently identified as acetylcholine, and also a product which causes rise in the blood pressure and is carried down by the precipitate when mercuric chloride is added to the extract. The latter substance is probably tyramine, but it could not be identified with certainty by reason of the small amount of available material; the benzoyl derivative which was only obtained in minimal amount had m. p. 165° (decomp.), whereas benzoyltyramine has m. p. 170°. It is very improbable that histamine is present. Chemical evidence of the presence of an alkaloid could not be obtained with the amount of substance available.

The isolation of choline and acetylcholine from the liquid extracts is described in detail; it is also shown that the choline bases can be directly obtained from such preparations by precipitation with alcoholic platinic chloride solutions without previous use of lead, mercury, or barium salts, and the following method of evaluating the extract is based on this observation. The extract (1 : 1; 5 c.c.) is mixed with spirit (12 c.c.) and treated with alcoholic platinic chloride solution (1%, 20—25 c.c.); the precipitate is filtered after one or two days, dried on the filter, and extracted with hot water, the impurities remaining on the filter. The filtrate is evaporated in a weighed dish. If necessary, the concentrated filtrate is again

filtered or, should it become turbid, it is precipitated with alcohol (70%). A good sample of the drug should yield at least 0·2 gram of platinum choline compounds; the purity of the isolated platinichlorides is controlled by observation of the melting point or by estimation of platinum or nitrogen. H. W.

The Active Constituents of *Capsella bursa pastoris*. H. W. van Urk (*Pharm. Weekblad*, 1921, **58**, 553—556).—Although the extract gives feeble reactions with iodine potassium iodide solution, Mayer's reagent, and tannin, no other alkaloid reactions could be obtained, and the effects cannot be ascribed to alkaloids. The presence of a glucoside is also doubtful, and the absence of allylthiocarbimide is confirmed. S. I. L.

The Alkaloids of Valerian. A. Goris and Ch. Vischniac (*Compt. rend.*, 1921, **172**, 1059—1061).—The authors confirm the work of Waliszewski (compare *Union pharm.*, 1893, **34**, 251) as to the existence of the two alkaloids chatinine and valerine in valerian root. One kilo. of fresh root only yielded 0·10 gram of mixed alkaloids, the chatinine predominating. W. G.

Constituents of the Bark of *Zanthoxylum macrophyllum*, Oliver. John Augustus Goodson (*Biochem. J.*, 1921, **15**, 123—128).—A review of the chemistry of nine species of this genus. The bark of *Z. macrophyllum* contains fagaramide and lupeol. Contrary to the statement of Thoms and Thümen (A., 1912, i, 115), the former substance is a feeble base, and yields a crystalline *hydrochloride*, $2C_{14}H_{17}O_3N,HCl$, m. p. 137°. G. B.

The Existence of Emulsin and of Lipase in Malt Extract. Marc H. van Laer (*Compt. rend. Soc. Biol.*, 1921, **84**, 471—472, 473—474; from *Chem. Zentr.*, 1921, i, 793).—It has been suggested that a diastatic extract may perform various fermentative actions according to the intensity of absorption. It is now shown that certain glucosides can be hydrolysed by malt extracts. The existence of a lipase is inferred from the fact that ethereal salts (ethyl acetate, ethyl butyrate, and amyl acetate) can be similarly hydrolysed. The optimum reaction for both hydrolyses is methyl-orange neutrality. G. W. R.

The Application of the van Slyke Method to Hydrolysed Protein Extracts of Silage Crops. Ray E. Neidig and Robt. S. Snyder (*J. Amer. Chem. Soc.*, 1921, **43**, 951—959).—From the analysis of a number of forage crops before and after conversion into silage, it would appear that the proteins of such crops, which contain such a large amount of cellulose, cannot be successfully analysed by the van Slyke method as applied directly to the hydrolysed extract of the original material. The new method of Eckstein and Grindley (A., 1919, ii, 204) gives results which permit of a fair interpretation of the protein molecule when applied to concentrates which contain but little cellulose. W. G.

Organic Chemistry.

Some Physical Properties of Hydrocarbons containing Two and Three Carbon Atoms. O. Maass and C. H. Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 1098—1111).—The authors have determined the melting point, vapour pressures at various temperatures, critical temperature, density at various temperatures, specific and molecular volumes, surface tension and molecular surface energy at various temperatures for ethane, ethylene, acetylene, propane, propylene, and allylene. Constant temperature baths for the temperature range 0 to −200° are described. The following values have been obtained. Melting points: ethane, −172·0°; ethylene, −169·4°; acetylene, −81·8°; propane, −189·9°; propylene, −182·5°, and allylene, −104·7°. Vapour pressure: allylene, −73·3°, 71·5 mm.; −41·20°, 408 mm.; −31·20°, 645 mm.; −21·30°, 992 mm.; ethane, −100·8°, 364·5 mm.; −95·5°, 504·0 mm.; −88·4°, 753·0 mm.; −72·7°, 1654·5 mm.; propane, −43·4°, 857 mm.; −23·1°, 2021 mm. Boiling points: ethane, −88·3°; ethylene, −103·9°; acetylene, −83·6°; propane, −44·5°; propylene, −47·0°; and allylene, −27·5°. Critical temperatures: ethane, 35·0°; ethylene, 9·9°; acetylene, 36·5°; propane, 95·6°; propylene, 92·1°; allylene, 127·9°. Density at the boiling point: ethane, 0·5459; propane, 0·5853; ethylene, 0·5699; propylene, 0·6095; acetylene, 0·6208; allylene, 0·6785. Surface tension at the boiling point: ethane, 16·05; ethylene, 16·50; acetylene, 19·58; propane, 15·63; propylene, 16·70; allylene, 18·57. The other values are recorded in long tables, and all values are discussed from the point of view of agreement between expected and observed results.
J. F. S.

Synthesis of some Branched-chain Hexanes. H. van Risseghem (*Bull. Soc. chim. Belg.*, 1921, **30**, 8—14).—Di*iso*propyl was synthesised from pinacolin by reducing it with hydrogen in presence of platinum black to the corresponding alcohol, dehydrating the latter with toluene-*p*-sulphonic acid to a mixture of two hexenes, one boiling at 55—57° and the other at 73°, isolating the latter (βγ-dimethyl-Δ^{β}-butylene) and reducing it with hydrogen in presence of platinum black to the required hexane. The following constants were determined: b. p. 58·05°/760 mm., m. p. −135·1°, D_4^0 0·6795, D_4^{15} 0·6659. *iso*Hexane, $CHMe_2\cdot CH_2\cdot CH_2Me$, was prepared by reducing mesityl oxide to methyl*iso*butylcarbinol, dehydrating as above to δ-methyl-Δ^{β}-pentene, b. p. 58—59°, and reducing with hydrogen and platinum black to the hexane. The following constants, differing from those previously given in the literature, were found: b. p. 60·2°, D_4^0 0·6712, D_4^{15} 0·6580. γ-Methylpentane was synthesised by hydrogenation of γ-methylpentene, b. p. 69—71°, D_4^{15} 0·7055, prepared from diethyl ketone

which was converted into methyldiethylcarbinol by the Grignard reaction and the latter distilled, when water and the hexene passed over. γ-Methylpentane has the following characters, differing from previous observations: b. p. 63·2°, D_4^{15} 0·6687, D_4^0 0·6820.

G. F. M.

A Paraffin Hydrocarbon contained in Commercial Benzene. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1920, **29**, 227—229).—A hydrocarbon consisting chiefly of n-heptane mixed with a small quantity of a C_7-polymethylene was separated from commercial benzene; the quantity of the hydrocarbon present is less than 0·3%, and it does not yield a sulphonic acid. W. P. S.

Shifting of the Ethylenic Bond in presence of Acid Catalysts. A. GILLET (*Bull. Soc. chim. Belg.*, 1920, **29**, 192—199).—The butylene obtained from n-butanol depends on the catalyst used; the author shows that this involves a secondary change, as the catalysts that yield *iso*butylene from butanol are also capable of forming this substance from n-butylene. Further, the change is a general one as $CHR^{IV}R^{V}\cdot CR^{III}:CR^{I}R^{II} \longrightarrow CR^{IV}R^{V}:CR^{III}\cdot CHR^{I}R^{II}$, when $R^{IV}R^{V}$ are more positive than $R^{I}R^{II}$. Certain exceptions to this general reaction have enabled the mechanism of the reaction to be investigated. H. J. E.

Action of $\beta\gamma$-Dibromopropylene on Magnesium *iso*Propyl Bromide. ROBERT LESPIEAU (*Compt. rend.*, 1921, **172**, 1236—1238. Compare A., 1920, i, 520).—Magnesium *iso*propyl bromide reacts with $\beta\gamma$-dibromopropylene in ethereal solution to give *β-bromo-δ-methyl-Δ^{α}-pentene*, b. p. 126—127°; D^{18} 1·207; n_D^1 1·4627, together with a *compound*, b. p. 63°/11 mm.; D^{24} 1·0942; n_D^{20} 1·456, which is probably γ-bromo-$\beta\gamma\epsilon$-trimethylhexane. With bromine, the bromomethylpentene yields *$\delta\delta\epsilon$-tribromo-β-methylpentane*, b. p. 116—117°/16 mm.; D^{17} 1·986; n_D^{17} 1·561, which with sodium ethoxide gives *$\alpha\beta$-dibromo-δ-methyl-Δ^{α}-pentene*, b. p. 70—71°/11 mm.; D^{17} 1·621; n_D^{17} 1·512. The latter compound, when warmed with zinc dust and alcohol, yields *δ-methyl-Δ^{α}-pentinene*, $CH:C\cdot CH_2\cdot CHMe_2$, b. p. 61·5—62°/760 mm.; D^0 0·7244, giving with silver nitrate in alcoholic solution a *silver* salt, $CAg:C\cdot CH_2\cdot CHMe_2,AgNO_3$.

W. G.

Oxidation of Diamylene. J. SCHINDELMEISER (*Chem. Zeit.*, 1921, **45**, 566).—The hydrocarbon was prepared from a mixture of β-methyl-Δ^{α}- and -Δ^{β}-butylenes and had b. p. 154—159°, D^{15} 0·770, n_D 1·4476. It was converted by potassium permanganate (3%) into acetic acid, an *acid*, b. p. 102—105°/20 mm. (the *copper* salt, $(C_8H_{15}O_2)_2Cu,5H_2O$, *silver* and *calcium* salts were prepared), an *acid* of higher boiling point (the crystalline *silver* salt, $C_9H_{17}O_2Ag$, of which was analysed) and succinic acid. The neutral portion of the oxidised substance contained a *ketone*, $C_7H_{14}O_2$, b. p. 147—149°, the *oxime* of which, $C_7H_{14}O:N\cdot OH$, had b. p. 101—102°/13 mm., D^{17} 0·9020, n_D 1·45789 and a fraction of higher boiling point which was separated by hydroxylamine into a nitrogen-free *sub-*

stance, $C_{10}H_{20}O$, b. p. 192—196°, D^{15} 0·9468, n_D 1·42642, and an *oxime*, C_9H_{18}:N·OH, b. p. 115—118°/12 mm., m. p. 83·5°. A *glycol*, $C_{10}H_{20}(OH)_2$, m. p. 117°, was also isolated. Oxidation with chromic acid yielded the same products with the exception of the glycol. H. W.

The Ethylenic Isomerism of Chlorobromoethylene. H. van de Walle (*Bull. Soc. chim. Belg.*, 1919, **28**, 369—375).—The mixture of stereoisomeric chlorobromoethylenes obtained by the chlorination of dibromoethylene with antimony pentachloride and subsequent reduction with zinc has been resolved into its components by fractional distillation of the material in the presence of alcohol. The *cis*-isomeride has b. p. 84·5—84·7°; D_4^{15} 1·7972; n_α^{15} 1·50472; n_D^{15} 1·49817; n_F^{15} 1·48143; and the *trans*-isomeride has m. p. 41°; b. p. 75·2—75·4°; n_α^{15} 1·50594; n_D^{15} 1·49976; n_F^{15} 1·48326. These two isomerides do not apparently undergo isomerisation in sunlight in the presence of a trace of bromine, but in diffused light the *cis*-isomeride shows an increase in its density and refractive indices, whilst the *trans*-isomeride shows a decrease. W. G.

αβ-Dichloro-α-bromoethylene. H. van de Walle (*Bull. Soc. chim. Belg.*, 1920, **29**, 166—169. Compare Swarts, A., 1899, i, 725).—A considerable quantity of the substance was fractionally distilled to obtain, if possible, the two stereoisomerides. A single substance was obtained, and further attempts at resolution into a mixture were unsuccessful. αβ-Dichloro-α-bromoethylene solidifies at −83·5°, b. p. 113·8°/760 mm.; D_4^{15} 1·9133; $n_{H_\alpha}^{15}$, 1·51795; n_D^{15}, 1·52188, n_F^{15} 1·53276. H. J. E.

Preparation of the Stereoisomerides of αβ-Dichloro-α-bromoethylene. H. van de Walle (*Bull. Soc. chim. Belg.*, 1920, **29**, 322—326).—Two stereoisomeric dichlorobromoethylenes were obtained by the reduction of dichlorotribromoethane by zinc in absolute alcoholic solution. They were separated as binary mixtures with alcohol by repeated fractional distillation of the product. The stable isomeride was identical with that previously obtained by the action of aniline on dichlorodibromoethane, and it formed a binary mixture with alcohol, b. p. 77·2—77·6°, containing 69·1% of alcohol. The unstable isomeride formed with 34·5% of alcohol a fraction boiling at 74·7—75·2°. The proportion of the isomerides formed was 72·4% of the unstable and 27·6% of the stable compound. On precipitating from the binary alcoholic mixture with water, the unstable stereoisomeride, which initially had μ_D 1·51592, rapidly changed to the stable compound having μ_D 1·52182. It was not possible to establish the spatial structure of the compounds by the action of alcoholic potassium hydroxide, as the velocity of attack was the same in each case, owing probably to rapid isomerisation. G. F. M.

αβ-Dichloro-αβ-dibromoethylene. H. van de Walle (*Bull. Soc. chim. Belg.*, 1920, **29**, 307—308).—αβ-Dichloroethylene was

converted by bromination in sunlight into αβ-dichloro-αβ-dibromoethane, which, on distillation with the theoretical amount of aniline, lost the elements of hydrogen bromide and gave αβ-dichloro-β-bromoethylene. On further bromination, *αβ-dichloro-αββ-tribromoethane* was obtained. It is a lachrymatory liquid having the following characters: b. p. 112°/16 mm., m. p. 5·95°, D_4^{15} 2·6346, μ_D 1·60846. It was converted by alcoholic potassium hydroxide into *αβ-dichloro-αβ-dibromoethylene*, CClBr:CClBr, b. p. 172°/760 mm., m. p. 4·4°, D_4^{15} 2·3036, μ_D 1·57984. The substance was a single chemical individual, representing only one of the two possible stereoisomerides. G. F. M.

The Chlorination of Acetylene Dibromide [αβ-Dibromoethylene] by Antimony Pentachloride. H. van de Walle (*Bull. Soc. chim. Belg.*, 1919, **28**, 304—309).—When antimony pentachloride is added drop by drop to αβ-dibromoethylene, a mixture of products is obtained, as follows:—*αββ-Trichloro-α-bromoethane*, $CHClBr\cdot CHCl_2$; b. p. 172° or 68°/22 mm.; $D_4^{14.5}$ 1·9592; $n_\alpha^{14.5}$ 1·52915; $n_D^{14.5}$ 1·53246; $n_\beta^{14.5}$ 1·54080; $n_\gamma^{14.5}$ 1·54787; *α-chloro-αββ-tribromoethane*, $CHClBr\cdot CHBr_2$, b. p. 220° (decomp.) or 97°/14 mm.; m. p. 20·55°; D_4^{14} 2·6518; n_α^{14} 1·60077; n_D^{14} 1·60527; n_β^{14} 1·61693; and αβ-dichloro-αβ-dibromoethane, CHClBr·CHClBr (compare Chavanne, A., 1912, i, 330). The first-named compound, when reduced by zinc, gives αβ-dichloroethylene, and the last, on reduction, gives a mixture of αβ-dichloro- and α-chloro-β-bromoethylene. In endeavour to find an explanation of the result of the second reduction, chloral was brominated by the action of bromine and phosphorus trichloride and the resulting trichlorodibromoethane reduced by zinc, when ααβ-trichloroethylene, $CHCl:CCl_2$, was obtained. Under similar conditions, dichloroacetaldehyde gave αα-dichloro-ββ-dibromoethane, which on reduction gave a mixture of αβ-dichloro- and α-chloro-β-bromo-ethylene. W. G.

Ethylenic Isomerism of the αβ-Dibromopropylenes. H. van Risseghem (*Bull. Soc. chim. Belg.*, 1919, **28**, 376—381).—By fractional distillation with alcohol of the mixture of stereoisomeric αβ-dibromopropylenes obtained by the action of sodium phenoxide on αββ-tribromopropane, the two isomerides have been separated after decomposing the proper binary mixtures with water. The *cis*-isomeride has b. p. 135·2°±0·2°/760 mm.; $D_4^{17.4}$ 2·0235; $n_\alpha^{17.4}$ 1·52935; $n_D^{17.4}$ 1·53371; and the *trans*-isomeride has b. p. 125·95°/760 mm.; $n_\alpha^{17.4}$ 1·53232; $n_D^{17.4}$ 1·53687. These two isomerides undergo isomerisation in sunlight in the presence of a trace of bromine to give an equilibrium mixture containing 35% of the *cis*-isomeride and 65% of the *trans*-isomeride. W. G.

Decomposition of some Metallic Alkyloxides and Phenoxides by Heat. J. F. Durand (*Compt. rend.*, 1921, **172**, 1504—1506).—Sodium methoxide when heated begins to decompose at about 300°, the reaction being $6CH_3\cdot ONa = 9H_2 + Na_2C_2 + 2Na_2CO_3 + 2C$, with a slight secondary action. Potassium methoxide behaves

similarly, but towards the end of the action there is liberation of some metallic potassium. Barium methoxide begins to decompose at 350° according to the equation $2(CH_3\cdot O)_2Ba = 6H_2 + BaO + BaCO_3 + 3C$. Sodium ethoxide decomposes according to the equations $2C_2H_5\cdot ONa = 2C_2H_4 + 2NaOH$, $2C_2H_5\cdot ONa = 4H_2 + 2NaOH + 4C$. Sodium phenoxide decomposes giving hydrogen, sodium hydroxide, and carbon. W. G.

Properties of Mixtures of *iso*Propyl Alcohol and Water. ROBERT B. LEBO (*J. Amer. Chem. Soc.*, 1921, **43**, 1005—1011).—The specific gravity of *iso*propyl alcohol and its mixtures with water has been determined at 20°; the following values of $D_{4°}^{20}$ are given for the various mixture: 100% alcohol, 0·78556; 90·35%, 0·80866; 85·09%, 0·82282; 74·35%, 0·84828; 65·22%, 0·87003; 53·07%; 0·89868; 43·02%, 0·92418; 33·17%, 0·94590; 21·39%, 0·96847; and 9·58%, 0·98293. A complete specific gravity table of mixtures of *iso*propyl alcohol and water has been drawn up from the above values. The boiling and condensing points of the mixtures have been determined. It is shown that the pure alcohol boils at 82·4° and the constant boiling mixture at 80·4°, this mixture has $D_{4°}^{20}$ 0·8158 and a weight composition 87·70% alcohol and a volume composition 91·09% alcohol. The boiling-point curves indicate that *iso*propyl alcohol is more easily rectified than ethyl alcohol. *iso*Propyl alcohol appears to hold water much less tenaciously than does ethyl alcohol. J. F. S.

Preparation of Secondary Butyl Alcohol. CHARLES WEIZMANN and DAVID ALLISTON LEGG (Brit. Pat. 161591).—Liquefied β-butylene is mixed with 75% sulphuric acid, with phosphoric acid, or with benzenesulphonic acid, either at the ordinary temperature under increased pressure or at −10° to −15° under atmospheric pressure. When absorption of the hydrocarbon is complete, the liquid is distilled with steam and pure *sec.*-butyl alcohol passes over. G. F. M.

The Action of Bromine on Allyl Phosphates in Aqueous Solution, and Transformation of Mono-allyl-phosphoric Acid into a Mono-glycero-mono-phosphoric Ester. OCTAVE BAILLY (*Bull. Soc. chim.*, 1921, [iv], **29**, 280—283. Compare A., 1916, i, 113).—The dibromo-additive product formed by disodium allyl phosphate gives, on heating in aqueous solution, first a monobromo-derivative of glycerophosphoric acid,

$$PO(ONa)_2\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2Br,$$

and finally an ester, $PO(ONa){<}{\begin{smallmatrix}O\cdot CH_2\\ O\cdot CH_2\end{smallmatrix}}{>}CH_2\cdot OH$, which is considered to have the αγ-constitution. H. J. E.

The Action of Epichlorohydrin on Disodium Hydrogen Phosphate in Aqueous Solution, and the Stability of a Mono-glycerol Monophosphoric Ester. OCTAVE BAILLY (*Bull. Soc. chim.*, 1921, [iv], **29**, 274—280).—See this vol., i, 299.

ββ′-Dichlorodiethyl Sulphide. M. DELÉPINE, FLEURY, and L. VILLE (*Compt. rend.*, 1921, **172**, 1238—1240).—Samples of ββ′-dichlorodiethyl sulphide prepared from ethylene and sulphur chloride are never pure. They contain a substance which, when distilled under reduced pressure, yields a small amount of hydrogen chloride, and they also contain substances which are apparently isomerides of ββ′-dichlorodiethyl sulphide. The sulphide cannot be used satisfactorily as a solvent for cryoscopic measurements.
W. G.

Some Physical Constants of ββ′-Dichlorodiethyl Sulphide. LEASON H. ADAMS and ERSKINE D. WILLIAMSON (*J. Washington Acad. Sci.*, 1919, **9**, 30—35).—The compressibility of ββ′-dichlorodiethyl sulphide at 31·5° is expressed by the equation $dv/dP = 49{\cdot}5e^{-0{\cdot}364\times10^{-3}P}$, from which the value at $P=0$, is found to be $49{\cdot}5\times10^{-6}$ per megabar, whilst at 1000 and 2000 megabars respectively the compressibility is $34{\cdot}4\times10^{-6}$ and $23{\cdot}9\times10^{-6}$. The dependance of freezing point on pressure has also been examined, and from the results thus obtained and the observed change of volume on freezing the latent heat of fusion is calculated to be 25 cal. per gram.
H. W.

The Preparation of Esters by Distillation of a Mixture of an Organic Acid and an Alcohol. H. WUYTS and R. BAILLEUX (*Bull. Soc. chim. Belg.*, 1920, **29**, 55—67).—The process of esterification is so conducted at the ordinary pressure, or under reduced pressure at such a temperature that only a portion of the products or one of the reacting substances is volatile. Two cases may occur, namely, (1) in which the ester is the most volatile component, (2) in which water and alcohol are the most volatile components and the organic acid the least volatile. In the first case, the ester distils off as formed, although the problem may be rendered more complex by the eventual formation of binary or ternary mixtures with low boiling points, which may facilitate the separation or render it more difficult. In the second case, it has been possible by this method to prepare esters which have previously had to be prepared from their components by heating them together in sealed tubes. In many cases, it is desirable to use *p*-toluenesulphonic acid as a catalyst. Numerous examples are given of esterifications by this method.
W. G.

Preparation of Chloroacetyl Chloride. E. DE BARRY BARNETT (*Chem. News*, 1921, **122**, 220).—The action of thionyl chloride on chloroacetic acid gives a 95% yield of chloroacetyl chloride if the process is continuous; it has b. p. 108—110°/764 mm., not "about 105°" (Beilstein, 4th edn., II, 199).
H. J. E.

Some Minimum Boiling-point Mixtures. FAILLEBIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 272—273. Compare Wade, Trans., 1905, **87**, 1656, and Merriman, Trans., 1913, **103**, 1790).—Water forms minimum boiling-point mixtures with the following esters: with ethyl benzoate, b. p. 98·5°; with *n*-butyl *n*-butyrate, b. p. 97°; with ethyl phenylacetate, b. p. 99·4°; with ethyl oxalate,

b. p. 97·5°. It is more difficult to determine the minimum boiling-point mixtures in the case of esters which are quite soluble in water. Alcohols and esters in some cases also form minimum boiling-point mixtures: methyl alcohol and ethyl acetate, b. p. 62·2°/769 mm.; *n*-butyl alcohol and *iso*butyl acetate, b. p. 113°/763 mm. The other determinations that have been carried out are: propyl acetate with 15·4% water, b. p. 83°/781 mm.; *n*-butyl acetate with 27·0% water, b. p. 90·5°/765 mm.; benzyl acetate with 87·0% water, b. p. 99·2°; *n*-propyl alcohol with 49·8% of *n*-propyl acetate, b. p. 94·8°/769 mm. H. J. E.

Acrylic Acid and Acrylic Esters. Halogenated Propionic Acids and Esters. CHARLES MOUREU, MARCEL MURAT, and LOUIS TAMPIER (*Compt. rend.*, 1921, **172**, 1267—1269. Compare this vol., i, 390).—Acraldehyde is saturated with dry hydrogen chloride at $-15°$ and the product is oxidised with nitric acid (D 1·49). When the resulting β-chloropropionic acid is warmed with aqueous sodium hydroxide, an excellent yield of acrylic acid is obtained. With the hydrogen haloids in the cold, acrylic acid gives β-halogenated propionic acids.

Acrylic esters may be prepared in some cases directly by heating together acrylic acid and the alcohol in the presence of sulphuric acid. A more general method is to warm the corresponding β-halogenated propionic ester with diethylaniline. The following esters are described: Methyl acrylate, b. p. 80·5°/761 mm.; D_4^{18} 0·9558; n_D^{18} 1·4117; methyl β-chloropropionate, b. p. 148—150°/760 mm.; D_4^{12} 1·1874; n_D^{12} 1·4319; *methyl β-bromopropionate*, b. p. 80°/27 mm.; D_4^{17} 1·4880; n_D^{17} 1·4603; ethyl acrylate, b. p. 99·8°/761 mm.; D_4^{18} 0·9238; n_D^{18} 1·4072; ethyl β-chloropropionate, b. p. 162·5°/761 mm.; D_4^{15} 1·1141; n_D^{15} 1·4284; ethyl β-iodopropionate, b. p. 116—117°/45 mm.; D_4^{15} 1·7040; *butyl acrylate*, b. p. 59°/25 mm.; D_4^{12} 0·9117; n_D^{12} 1·4254; *butyl β-bromopropionate*, b. p. 122·5°/18 mm.; D_4^{9} 1·2773; n_D^{9} 1·4577; iso*amylacrylate*, b. p. 71—72°/22 mm.; D_4^{12} 0·9070; n_D^{12} 1·4287; iso*amyl β-bromopropionate*, b. p. 110—111°/11 mm.; D_4^{9} 1·2320; n_D^{9} 1·4556; *benzyl acrylate*, b. p. 110—111°/8 mm.; D_4^{8} 1·0690; n_D^{8} 1·5232; *menthyl acrylate*, b. p. 128°/18 mm.; D_4^{15} 0·9310; n_D^{15} 1·4624. W. G.

The Decomposition of Oxalates. M. HERSCHKOWITSCH (*Zeitsch. anorg. Chem.*, 1921, **115**, 159—167).—When ferrous oxalate is decomposed by heat in absence of air, the residue contains about half the iron as metal, the remainder as ferrous oxide; a mixture of carbon monoxide and carbon dioxide is evolved, and a small amount of carbon also appears in the residue. In the case of nickel oxalate, the residue is almost pure metallic nickel, with very small quantities of oxide and carbonate, whilst the gaseous product is mainly carbon dioxide with very little monoxide. Probably with all oxalates the primary decomposition products are metal and carbon dioxide, but the readily oxidisable metals such as sodium, potassium, or calcium reduce half of the carbon dioxide, the final products being carbonate and carbon monoxide. Part of the carbon dioxide may be reduced to carbon, and in consequence

a small amount of metallic oxide remains uncombined. Less readily oxidisable metals such as iron or lead reduce only a part of the carbon dioxide, and a mixture of metal and metallic oxide is found in the residue. In the case of lead oxalate, the oxide formed is the suboxide. Calorimetric experiments were made on the residue from lead oxalate, and the heat of solution of lead suboxide in acetic acid according to the equation $Pb_2O+2AcOH=Pb(OAc)_2+Pb+H_2O$ was found to be 16,710 cal., whilst the corresponding heat of solution of litharge was found to be 15,500 cal. The heat of decomposition of lead suboxide into lead and litharge, $Pb_2O=Pb+PbO$, is therefore 1210 cal., and not a negative quantity, as found by Tanatar (A., 1901, ii, 451). The heat of formation of lead suboxide from its elements is 49,190 cal.

E. H. R.

Formation and Stability of *spiro*-Compounds. IV. Ketones Derived from Open-chain and Cyclic Glutaric Acids. GEORGE ARMAND ROBERT KON (Trans., 1921, **119**, 810—830).

Undecamethylenedicarboxylic Acid as a Degradation Product of Oleic Acid. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1921, **114**, 28—30).—The so-called "oily acid" of wool-fat (*ibid.*, 1920, **110**, 29) is considered to be identical with a product obtained by the oxidation of oleic acid in glacial acetic acid solution by means of permanganate (A., 1908, i, 263). This wax-like oxidation product, purified by repeated precipitation from its calcium salt and melting at 82—85°, is further considered to be identical with an undecamethylenedicarboxylic acid (m. p. 81—82° after distillation and crystallisation) obtained by Komppa (A., 1901, i, 365). In spite of the method of synthesis, Komppa's acid was not identical with *n*-undecane-$\alpha\lambda$-dicarboxylic acid=brassylic acid, m. p. 112°.

C. R. H.

Chemistry of Aconitic Acid. I. The Preparation and Properties of the Hydroxy-anhydro-acid. P. E. VERKADE (*Rec. trav. chim.*, 1921, **40**, 381—386).—When aconitic acid is heated with acetyl chloride or with acetic anhydride, the first product is the hydroxy-anhydro-acid (Bland and Thorpe, Trans., 1912, **101**, 1490), whether the reagent contains phosphorus trichloride or not. If the boiling be prolonged, the hydroxy-anhydro-acid then passes into the normal anhydro-acid. This change is catalytically accelerated by phosphorus trichloride, and this explains why Bland and Thorpe obtained the hydroxy-anhydro-acid only by the use of acetyl chloride free from phosphorus trichloride, since they heated aconitic acid with the reagent for a period considerably longer than is necessary for the formation of the initial dehydration product.

C. K. I.

The Formation of Dibutylbutylal in the Preparation of Butyl Alcohol by Hydrogenation of Crotonaldehyde. H. VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1919, **28**, 335—339).—Amongst the products of hydrogenation of crotonaldehyde, by passing its vapour along with hydrogen over reduced nickel at 130°, the author

has obtained a considerable amount of *dibutylbutylal*, $CHPr(O\cdot CH_2Pr)_2$, b. p. 105—109°/18 mm.; $D_4^{14\cdot6}$ 0·8589; $D_4^{17\cdot5}$ 0·8578; $n_\alpha^{14\cdot6}$ 1·4213; $n_D^{14\cdot6}$ 1·4234; $n_\beta^{14\cdot6}$ 1·4289; $n_\alpha^{17\cdot5}$ 1·4189; $n_D^{17\cdot5}$ 1·4211; $n_\beta^{17\cdot5}$ 1·4262. This butylal may also be prepared by heating together butyl alcohol and butaldehyde in the presence of a little toluenesulphonic acid.

W. G.

Two New Derivatives of α- and β-Methylglucoside. BURCKHARDT HELFERICH (*Ber.*, 1921, **54**, [*B*], 1082—1084).—A method for the direct replacement of hydroxyl groups by halogen atoms in glucosides has not been published previously. It is shown that two hydroxyl groups of α-methylglucoside are replaced by chlorine atoms and the remaining two are esterified by the sulphuric acid radicle when the substance is added to a freshly-prepared mixture of dry chloroform, anhydrous pyridine, and sulphuryl chloride; *α-methylglucoside dichlorohydrin sulphate* crystallises in well-defined needles, m. p. 104—105°, $[\alpha]_D^{17}+139\cdot97°$, in glacial acetic acid solution. It reduces Fehling's solution only after being hydrolysed with mineral acid. *β-Methylglucoside dichlorohydrin sulphate* has m. p. 137° (slight decomp.), $[\alpha]_D^{19}-11\cdot84°$, in glacial acetic acid solution. The reaction depends greatly on manipulative details; it can be applied to di- and poly-saccharides and their glucosides. H. W.

The Configuration of some Sugars. J. BÖESEKEN and H. COUVERT (*Rec. trav. chim.*, 1921, **40**, 354—380).—The method already described and illustrated (A., 1913, i, 1147; ii, 147, 742; 1915, ii, 136, 617, 668; 1916, i, 596; ii, 73, 209, 595; 1917, ii, 146, 147; 1919, i, 412; 1920, ii, 219), by which information may be obtained regarding the constitutions of hydroxy-compounds from their effect on the conductivity of solutions of boric acid, has now been re-examined and applied to certain compounds of the sugar group.

The methyl derivatives of dextrose, α- and β-methylglucosides, tetramethylglucose, and tetramethyl-α- and -β-methylglucosides, which do not contain the two hydroxyl groups necessary for the formation of the compounds with boric acid to which the observed effects are ascribed, were submitted to measurement, with results which are considered to support the basic assumptions of the method.

The series of measurements previously made (A., 1916, i, 596) with α-*d*-glucose and α-*l*-fructose have now been amplified, and it is shown that, whilst α-*l*-arabinose and α-*l*-xylose behave like α-*d*-glucose, α-*l*-rhamnose and α-*l*-mannose resemble α-*l*-fructose. From measurements with sucrose, it is concluded that the fructose residue cannot be present in the form suggested by Haworth and Law (Trans., 1916, **109**, 1314) and the alternative form containing a propylene oxide ring is proposed. Since the compound of fructose and boric acid is a much stronger acid than boric acid itself, the inversion of sucrose by boric acid is an autocatalytic process as conductivity measurements show (compare *Versl. K. Akad. Wetensch. Amsterdam*, 1917, **26**, 3).

Details for titrating boric acid in the presence of invert-sugar

(compare A., 1920, ii, 331) are given, and it is shown that, in 0·1*N*-solution, using barium hydroxide and phenolphthalein as indicator, very accurate results may be obtained provided the molecular ratio of lævulose to boric acid is about 5 to 1. C. K. I.

Preparation of Lævulose-monophosphoric Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 334250; from *Chem. Zentr.*, 1921, ii, 961).—*Lævulose-diphosphoric acid* or its salts are heated with dilute acids until one molecule of phosphoric acid is split off. For example, the insoluble calcium salt of lævulose-diphosphoric acid is changed into the *calcium* salt of *lævulose-monophosphoric acid*, $C_6H_{11}O_5\cdot PO_4Ca,H_2O$, soluble in water but precipitable by ethyl alcohol. Lævulose-monophosphoric acid, obtained from lævulose-diphosphoric acid, gives with phenylhydrazine an *osazone*, $C_{24}H_{31}O_7N_6P$, in large sheaves or druses, m. p. 153°. G. W. R.

The Influence of Ammonium Molybdate on the Rotatory Power of some Sugars. GEORGES TANRET (*Compt. rend.*, 1921, **172**, 1363—1365).—Further measurements of the influence of ammonium molybdate on the rotatory power of some sugars are given. In the case of xylose, $[\alpha]_D$ passed from $+19\cdot2°$ to $+33\cdot5°$; arabinose, $[\alpha]_D$ fell from $+105°$ to $+84\cdot9°$; dextrose, $[\alpha]_D+52\cdot5°$, increased to $+54\cdot1°$; galactose, $[\alpha]_D+82\cdot5°$, fell to $+60°$; sorbose, $[\alpha]_D-43\cdot2°$, fell to $-36\cdot3°$; lævulose, $[\alpha]_D-90°$, fell to $-50°$; mannose, $[\alpha]_D$ passed from $+14°$ to $-20°$. In the case of the C_{12}, C_{18}, and C_{24} sugars and inulin, ammonium molybdate had no influence on the rotatory power. It is suggested that this effect of ammonium molybdate on the rotatory power of some sugars might form the basis of a rapid method for estimating one known hexose sugar in a mixture with other sugars on the rotatory power of which the molybdate had no influence. W. G.

Synthesis of Fatty Acid Derivatives of the Sugars. GÉZA ZEMPLÉN (*Ber.*, 1921, **54**, [*B*], 980).—In their recent communication on this subject (this vol., i, 305), Hess and Messmer have omitted any reference to the author's work in this field (A., 1915, i, 651). H. W.

Starch. A. REYCHLER (*Bull. Soc. chim.*, 1921, [iv], **29**, 311—316.—Compare Maquenne and Roux, A., 1906, i, 327, 547). —Preliminary experiments seem to show that starch grains consist of at least two substances, amylose and amylopectin, the former composing the interior of the grain, the latter being found in the wall. The stability of the grain as a whole towards certain reagents is discussed. H. J. E.

Application of the Biochemical Method of Detection of Dextrose to the Study of the Products of the Enzyme Hydrolysis of Inulin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1921, **172**, 946—949).—Using the method previously described (A., 1920, ii, 337) for the detection of dextrose, the authors were

not able to detect any dextrose in the products of hydrolysis of inulin by the inulase of *Aspergillus niger*. Inulin is thus a product of the condensation of lævulose molecules only. W. G.

The Hydrolysis of Cotton Cellulose. GORDON WICKHAM MONIER-WILLIAMS (Trans., 1921, **119**, 803—805).

The Cellulose of Lichens and Yeast; the Concept "Hemicellulose" and the Autolysis of Yeast. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1921, **114**, 31—38).—The cellulose of *Cetraria islandica* is found to be very easily hydrolysed, yielding 64·86% of dextrose. Schulze's "hemicellulose" theory is criticised, and, as the result of hydrolysis experiments with the same yeast cellulose after different preliminary treatment, it is suggested that the expression should be applied with caution, and only to the case of celluloses of indubitable purity.

Yeast cellulose is separated, by prolonged heating with water under pressure, into an insoluble achroocellulose and a soluble erythrocellulose; the latter substance, which gives an intense iodine reaction, is apparently identical with the so-called "yeast glycogen." The dextrose which is formed by the autolysis of yeast originates entirely from the erythrocellulose. C. R. H.

Some Methylated Amino-acids and Aporrhegmata, and their behaviour in the Animal Body. D. ACKERMANN and F. KUTSCHER (*Zeitsch. Biol.*, 1920, **72**, 177—186).—By methylation with barium hydroxide and methyl sulphate at the ordinary temperature, the authors have prepared *N*-trimethyl-α-alanine (α-homobetaine); N-*trimethylserine* (*aurichloride*, $C_6H_{14}O_3NAuCl_4$, m. p. 211—212°); N-*trimethylglutamic acid* (*aurichloride*, m. p. 135°); δ-*hydroxytrimethylammoniovaleric acid*, $OH\cdot NMe_3\cdot[CH_2]_4\cdot CO_2H$, from δ-aminovaleric acid (*aurichloride*, m. p. 165—166°); ε-*hydroxytrimethylammoniohexoic acid* from ε-aminohexoic acid (*aurichloride*, m. p. 152°) *phenylethyltrimethylammonium hydroxide*, $OH\cdot NMe_3\cdot CH_2\cdot CH_2Ph$, from phenylethylamine (*aurichloride*, m. p. 150); hexamethyltetramethylene diammonium hydroxide from putrescine; *hexamethylpentamethylenediammonium hydroxide*, $CH_2(CH_2\cdot CH_2\cdot NMe_3\cdot OH)_2$ from cadaverine and β-*iminazolylethyltrimethylammonium hydroxide* from histamine (*aurichloride*, $C_{10}H_{21}N_3Au_2Cl_8$, m. p. 227°). The aurichlorides are generally sparingly soluble in water. All these methylated substances have a pronounced curare-like action and resist oxidation in the organism; some at least passes unchanged into the urine. G. B.

The Products of Condensation of Carbamide and Formaldehyde. MARC VAN LAER (*Bull. Soc. chim. Belg.*, 1919, **28**, 381—392).—The condensation of formaldehyde and carbamide is much more complex and varied than are the condensations of formaldehyde with amines or amino-acids. At the ordinary temperature, the condensation affects the two amide groups, a symmetrical methylenic derivative being obtained, which then tautomerises, giving an asymmetric derivative, $NH_2\cdot CO\cdot N{:}CH_2$, or its

hydrate. Under other conditions, the change may be more complex, involving both the amide and the aldehyde hydrogen. This occurs if the temperature is raised or the carbamide is replaced by *s*-dimethylcarbamide, and under these conditions, according to the relative amounts of the two reagents used, insoluble bases with high molecular weights are formed, having the constitution of methylenic tricarbimides of the type $C_{12}H_{20}O_5N_{10}$ or $(C_{10}H_{16}O_5N_6)_x$ or $(C_{14}H_{20}O_7N_6)_x$. W. G.

Syntheses of Cyanic Acid and Carbamide by Oxidation of Ketones, Acids, and Amines in Presence of Ammonia. R. Fosse and G. Laude (*Compt. rend.*, 1921, **172**, 1240—1242).—Cyanic acid and subsequently carbamide have now been obtained by the oxidation in the presence of ammonia of ketones, mono- and di-basic acids, phenols, alcohols, and amines. The yield of carbamide varies considerably with the substance used, and, in the case of amines, those capable of giving formaldehyde by oxidation give the highest yield of carbamide. W. G.

Preparation of Guanidine Salts and of Nitroguanidine. Thomas Ewan and John H. Young (*J. Soc. Chem. Ind.*, 1921, **40**, 109—112_T).—It is shown that guanidine nitrate can be obtained in about 50% yield from sodium cyanamide, and that the loss occurs almost entirely in the last stage of the operation, which consists in the polymerisation of the cyanamide and its action on ammonium nitrate at 150—180°. Excellent yields of guanidine salts can be obtained by heating dicyanodiamide with the requisite ammonium salts and the preparation by this method of the nitrate, thiocyanate (compare Werner and Bell, Trans., 1920, **117**, 1133), sulphate, and hydrochloride are described in detail. Nitroguanidine is formed from guanidine nitrate by the action of sulphuric acid, nitric acid, or a mixture of the two acids; the first method is the most satisfactory, and the process is suitably conducted by allowing guanidine nitrate (5 grams) to remain in contact with sulphuric acid (92—98%, 5 c.c.) during forty-eight hours, after which the mixture is poured into so much water that the solution ultimately contains 20% of sulphuric acid. H. W.

Preparation of Cyanogen Chloride. Emilio Sernagiotto (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 153).—Cyanogen chloride may be prepared in good yield by the interaction of chlorine and hydrocyanic acid in presence of animal charcoal as catalyst. To prevent polymerisation of the cyanogen chloride, the hydrogen chloride formed at the same time must be completely removed by passing the mixed gases through a tower charged with moistened marble, the carbon dioxide thus liberated escaping when the cyanogen chloride is condensed by means of ice. T. H. P.

The Bucher Cyanide Process for the Fixation of Nitrogen. Eugen Posnjak and H. E. Merwin (*J. Washington Acad. Sci.*, 1919, **9**, 28—30).—Microscopical examination of technical speci-

mens of sodium cyanide obtained by Bucher's process (ignition of a mixture of sodium carbonate and carbon with iron as catalyst in a current of nitrogen) showed that the nitrogen-bearing constituent sometimes consisted of some substance other than ordinary sodium cyanide. The latter is an essentially isotropic substance, crystallising in cubes and having n_D 1·452±0·003. After this cyanide has been fused, slight double refraction amounting to about 0·005 is observed. The material found in the technical products appeared in weakly doubly-refracting, colourless grains about 0·03 mm. in diameter. The refractive indices were $n_\alpha=1{\cdot}527$, $n_\beta=1{\cdot}532$, $n_\gamma=1{\cdot}537$. Attempts to prepare this substance by small scale experiments according to Bucher's method were unsuccessful, sodium cyanide being produced; it could not be isolated by distillation of the technical product at a temperature considerably above that at which sodium cyanide volatilises. H. W.

The Alkali Cyanides. JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1921, **115**, 203—217).—Methods have been devised for preparing the hitherto unknown cyanides of lithium, rubidium, and cæsium in a pure state. *Lithium cyanide* was prepared by shaking a suspension of finely crystalline, dry lithium hydroxide in ether with anhydrous hydrocyanic acid. The cyanide is extremely soluble in water, and resembles sodium and potassium cyanides in its properties. With silver cyanide, it forms *lithium silver cyanide*, $LiAg(CN)_2$, colourless crystals, which in aqueous solution does not react with hydrochloric acid, hydriodic acid, or disodium phosphate, but does so with hydrogen sulphide. *Lithium ferrocyanide* was prepared from hydroferrocyanic acid and lithium carbonate. It forms bright yellow crystals containing $6H_2O$, differing in this respect from the sodium salt. *Lithium ferricyanide*, prepared from silver ferricyanide and lithium chloride, is less soluble than the ferrocyanide, and forms an orange-red, crystalline powder containing $4H_2O$. *Rubidium cyanide* is very soluble in water, but is not hygroscopic; it is insoluble in alcohol and ether. It forms the double salt, $RbAg(CN)_2$, with silver cyanide. *Rubidium ferrocyanide* crystallises with $3H_2O$, and the *ferricyanide* and *manganicyanide* form anhydrous crystals, these salts being probably isomorphous with the corresponding potassium salts. *Cæsium cyanide*, and the salts $CsAg(CN)_2$, $Cs_4Fe(CN)_6,3H_2O$, and $Cs_3Fe(CN)_6$ were prepared and found to have similar properties to the corresponding rubidium salts.

All the alkali cyanides are hydrolysed by water and smell of hydrocyanic acid when exposed to the air. Determinations of the degree of hydrolysis at 18° and 25° in aqueous solution at dilutions from N to $N/10$ were made by measuring the rate of hydrolysis of methyl acetate. All five alkali cyanides were found to be hydrolysed to the same extent, namely about 1·25% at 25° in $N/10$-solution, or 0·4% in normal solution. E. H. R.

Dithiocarbazinic Acid. SIMA M. LOSANITCH (Trans., 1921, **119**, 763—765).

***n*-Amylbenzene and some of its Derivatives.** L. GUY RADCLIFFE and N. SIMPKIN (*J. Soc. Chem. Ind.*, 1921, **40**, 119—122$_T$).—*n*-Amylbenzene, b. p. 200·5—202°/761·2 mm., $D_{15·5}^{15·5}$ 0·8664, $D_4^{15·5}$ 0·8651, D_{22}^{22} 0·8624, D_4^{22} 0·8602, n_D^{15} 1·4751, is obtained in 27·6% yield by the action of sodium on benzyl bromide or chloride and *n*-butyl bromide; the metal should be added gradually to the well-stirred mixture of haloids containing a slight excess of the butyl derivative, dilution with benzene should be avoided, and the mixture should be kept as cool as is compatible with the continuance of the reaction, whilst it is advisable to allow it to remain for a few days at the ordinary temperature to complete the reaction. The substance is prepared in considerably better yield from *n*-amyl bromide and bromobenzene. n-*Amylbenzene*-p-*sulphonic acid*, hygroscopic needles, is obtained by the action of concentrated sulphuric acid on the hydrocarbon, and is isolated as the *barium* salt, colourless, prismatic crystals (the *potassium*, *silver*, and *calcium* salts were also prepared). The corresponding *sulphonyl chloride* forms flat, needle-shaped crystals, m. p. 38—39°, whereas the *sulphonamide*, colourless, hair-like crystals, has m. p. 86—87°, and is oxidised by potassium permanganate in boiling alkaline solution to *p*-sulphaminobenzoic acid, m. p. 278—280° (decomp.). Potassium *n*-amylbenzene-*p*-sulphonate is transformed by fusion with potassium hydroxide into n-*amylphenol*, b. p. 262° (*benzoate*, colourless needles, m. p. 52°, *bromo*-derivative, m. p. 88—89°). p-*Nitro*-n-*amylbenzene*, a yellow liquid, b. p. 158—159°/14 mm., is obtained by the action of nitric acid (D 1·508) and glacial acetic acid on the hydrocarbon. H. W.

The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. I and II. WILLIAM DAVIES (Trans., 1921, **119**, 853—875, 876, 876—887).

The Formation of Hexachlorobenzene in the Electrolytic Preparation of Chlorine. F. BOURION and CH. COURTOIS (*Compt. rend.*, 1921, **172**, 1365—1367).—In the pipes leading away the chlorine from the electrolytic cells in its industrial preparation, the authors have found considerable amounts of a white, crystalline substance. This is shown to be hexachlorobenzene, together with some less highly chlorinated derivatives of benzene. These chloro-compounds are probably formed from the tars used in the manufacture of the carbon anodes. W. G.

Halogen Derivatives of Methylethylbenzene. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1921, [iv], **29**, 290—294).—The action of chlorine on *m*-methylethylbenzene yields 6-*chloro*-m-*methylethylbenzene*, a liquid, b. p. 200—202°; the 4 : 6-*dichloro*-derivative forms colourless needles, m. p. 126°, b. p. 180°/60 mm.; the 2 : 4 : 6-*trichloro*-derivative crystallises in needles, m. p. 205°; the *tetrachloro*-derivative forms needles, m. p. 158°. Bromine forms 6 bromo-*m*-methylethylbenzene, a liquid, b. p. 220—221°; and the 4 : 6-*dibromo*-derivative, crystallising in needles, m. p. 210°.
H. J. E.

The Nitration Products of *p*-Dichlorobenzene. A. F. HOLLEMAN, A. I. DEN HOLLANDER, and F. E. VAN HALFTEN (*Rec. trav. chim.*, 1921, **40**, 323—326).—An examination has been made of the nitration product, prepared by Jungfleisch's method (*Ann. Chim. Phys.*, 1868, [iv], **15**, 259) of *p*-dichlorobenzene. If, after removing as much 2 : 5-dichloro-1 : 3-dinitrobenzene and 3 : 6-dichloro-1 : 2-dinitrobenzene as possible, by crystallisation, the residue be treated with cold alcoholic ammonia, 4-chloro-2 : 6-dinitroaniline separates. More energetic treatment with the same reagent converts the remaining 3 : 6-dichloro-1 : 2-dinitrobenzene into 3 : 6-dichloro-2-nitroaniline, from which the residual 2 : 5-dichloro-1 : 4-dinitrobenzene may be easily removed. Occasionally, the original nitration product contains 2 : 5-dichloronitrobenzene, which interferes with the separation of the dinitro-derivatives. (Compare A., 1920, i, 538.) C. K. I.

The Anthracene Series. I. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (Trans., 1921, **119**, 901—913).

The Condensation of Benzene and Chloral Hydrate in the Presence of Aluminium Chloride. MARC VAN LAER (*Bull. Soc. chim. Belg.*, 1919, **28**, 346—350).—Tri-α-chloro-di-β-phenylethane, obtained as one of the products of condensation of benzene and chloral hydrate in the presence of aluminium chloride, apparently undergoes partial condensation, giving a resin which has the constitution of a hydrochloride of bis-di-α-chloro-di-β-phenylethylbenzene, $C_6H_4(CCl_2{\cdot}CHPh_2)_2$. At the same time, some of the trichlorodiphenylethane condenses with more benzene to give *α-chloro-ααββ-tetraphenylethane*, $CHPh_2{\cdot}CPh_2Cl$. W. G.

Determination of the Configuration of Stereoisomeric Polymethylenes. A. SKITA (*Zeitsch. angew. Chem.*, 1921, **34**, 230—231).—A continuation of previous work (A., 1920, i, 27, 607, 832).—[*With* H. KADEN.]—*m*-4-Xylidine is converted by hydrogen and colloidal platinum into a mixture of cis-2 : 4-*dimethyl*cyclo*hexylamine*, b. p. 16·75°, D_4^{20} 0·862, n_D^{20} 1·4573, and trans-2 : 4-*dimethyl*cyclo*hexylamine*, b. p. 16·5°, D_4^{20} 0·853, n_D^{20} 1·4501, which are separated from one another in the form of their *benzoyl* derivatives, m. p. 86° and 198° respectively. The configuration of these compounds is proved by the observation that *m*-4-xylenol (prepared from the xylidene) is smoothly transformed into 1 : 3-dimethyl-4-*cyclo*hexanone, the *oxime* of which, m. p. 96°, is reduced in an acid medium to the base giving the benzoyl derivative, m. p. 86°, whilst in an alkaline medium the amine corresponding with the benzoyl derivative, m. p. 198°, is produced. Protracted catalytic reduction of *m*-4-xylenol at the ordinary temperature leads exclusively to the production of trans-1 : 3-*dimethyl*cyclo*hexane*, b. p. 119°, D_4^{20} 0·772, n_D^{20} 1·4254, the configuration of which is deduced from comparison with other members of the series and from the difference in its physical constants from those of cis-1 : 3-*dimethyl*cyclo*hexane*, b. p. 121°, D_4^{20} 0·774, n_D^{20} 1·4269, prepared from *m*-xylene in the presence of hydrochloric acid. It follows, therefore, that

the methyl groups of the xylidenes and xylenols just described are also in the *trans*-position to one another. [Hence *cis*-1 : 3-dimethyl-4-*cyclo*hexanol has b. p. 176°, D_4^{20} 0·907, n_D^{20} 1·4582, and yields an oily phenylurethane, whilst *trans*-1 : 3-dimethyl-4-*cyclo*hexanol has b. p. 175°, D_4^{20} 0·900, n_D^{20} 1·4560 (*phenylurethane*, m. p. 96°).] The decision as to the relative position of the methyl- and amino-groups is based on the observation (see later) that the differences between the physical constants of *cis*- and *trans*-1 : 2-substituted amines are considerably greater than those between the corresponding 1 : 4-compounds. Hence the *cis*-amine is to be regarded as *cis*-4-amino-*trans*-1-*cis*-3-dimethyl*cyclo*hexane, and the *trans*-amine as *cis*-4-amino-*cis*-1-*trans*-3-dimethyl*cyclo*hexane.

[*With* HANS HÄUBER.]—The theoretically possible methyl*cyclo*hexylamines and methyl*cyclo*hexanols have been prepared. cis-2-*Methyl*cyclo*hexylamine* has b. p. 153—154°, D_4^{20} 0·877, n_D^{20} 1·486° (*benzoyl* derivative, m. p. 107°) whilst the corresponding *trans*-compound has b. p. 149—150°, D_4^{20} 0·860, n_D^{20} 1·465, whereas cis-4-*methyl*cyclo*hexylamine* has b. p. 152—153°, D_4^{20} 0·858, n_D^{20} 1·457 (*benzoyl* derivative, m. p. 116—117°), and the corresponding *trans*-isomeride has b. p. 151—152°, D_4^{20} 0·847, n_D^{20} 1·451.

[*With* W. SCHNEIDER.]—*m*-2-Xylenol is converted into 1 : 3-dimethyl-2-*cyclo*hexanone, which gives only one alcohol when reduced in acid or alkaline solution, and only one amine when its oxime is treated similarly; this result is only possible if the two methyl groups are in the *trans*-position to one another. H. W.

Some Properties of Tetranitroaniline (TNA). B. J. FLÜRSCHEIM (*J. Soc. Chem. Ind.*, 1921, **40**, 97—107$_T$).—An extended account of the behaviour of tetranitroaniline when subjected to the different official tests for explosives is given. It is neutral and without action on metals. It is the strongest solid explosive, has a higher density than any other purely organic explosive, is non-hygroscopic, and does not change on storage. It is particularly resistant to heat and friction, not over-sensitive to mechanical shock, and can be easily detonated by an ordinary detonator, even when highly compressed. It has a smaller oxygen deficiency than other aromatic explosives and is a very suitable ingredient of explosive mixtures. H. W.

Preparation of Mixed Secondary and Tertiary Phenolic Amines. A. MAILHE and F. DE GODON (*Compt. rend.*, 1921, **172**, 1417—1419).—The method previously described (A., 1918, i, 217, 218) for the methylation of aniline and its homologues is equally applicable to their ethylation, the aniline and ethyl alcohol vapours being passed together over aluminium oxide at 350—380°. Aniline does not undergo such complete ethylation as its homologues. The method may also be used for converting diphenylamine into methyl- or ethyl-diphenylamine. W. G.

Improvements in the Manufacture of certain Naphthylamine-sulphonic Acids. SOUTH METROPOLITAN GAS COMPANY and HAROLD STANIER (Brit. Pat. 161859).—The separation of α-naph-

thylamine-4 : 8- and -3 : 8-disulphonic acids from the crude mixture obtained by the sulphonation of naphthylamine is effected by taking advantage of the differences in solubility of their barium salts. A suitably concentrated solution of the disodium salts is boiled with the calculated quantity of barium chloride sufficient to convert all the acids into their barium salts. Barium α-naphthylamine-4 : 8-disulphonate is precipitated, and the liquid is filtered hot. The filtrate and washings are acidified with hydrochloric acid, whereby the acid barium salt of the 3 : 8-acid is precipitated, and filtered off hot to secure retention in solution of the corresponding salts of the β-4 : 7- and β-4 : 8-acids which may be present. G. F. M.

Reduction of Emulsified Nitro-compounds. I. β-Phenyl-hydroxylamine from Nitrobenzene. ARTHUR LAPWORTH and LEONORE KLETZ PEARSON (Trans., 1921, **119**, 765—768).

Reduction of Emulsified Nitro-compounds. II. Some Extensions of the Method. ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH (Trans., 1921, **119**, 768—777).

The Transformation of Phenol into *cyclo*Hexanol. G. VAVON and J. DETRIE (*Compt. rend.*, 1921, **172**, 1231—1233).—In the hydrogenation of phenol in the presence of platinum black, the yield of *cyclo*hexanol varies but little with the experimental conditions. The velocity of the reaction is high. It is shown that *cyclo*hexanol is produced for the most part through the intermediate formation of *cyclo*hexanone, and not directly from the phenol. W. G.

Univalent Oxygen. Preparation and Oxidation of Mesitol. C. W. PORTER and F. H. THURBER (*J. Amer. Chem. Soc.*, 1921, **43**, 1194—1198).—In benzene solution, mesitol is oxidised by moist silver oxide at 50° to give a red, crystalline *compound*, 224—226°, which is unsaturated and is readily reduced to colourless products. Its reduction is accomplished by half the quantity of reducing agent that would be required if all the oxygen were quinone or peroxide oxygen. Molecular weight determinations indicate that it contains two mesitol nuclei. The properties of the compound are accounted for on the basis of a formula containing an oxidised mesitol residue possessing either univalent oxygen or tervalent carbon more or less firmly linked to an unoxidised molecule of the mesitol. W. G.

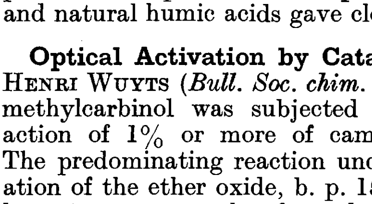
Preparation of Trinitroresorcinol. WALTER FRIEDERICH (Brit. Pat. 162578).—Trinitroresorcinol is obtained by allowing 90—100% nitric acid to flow with moderate cooling and brisk stirring into a suspension of resorcinoldisulphonic acid in concentrated sulphuric acid, the temperature being maintained between 30° and 80° during nitration. The crude product is yellowish-brown in colour and has m. p. 173—175°. G. F. M.

2 : 4 : 6-Trinitroresorcinol [Styphnic Acid]. HANS EINBECK and LUDWIG JABLONSKI (*Ber.*, 1921, **54**, [*B*], 1084—1089).—2 : 4 : 6-Trinitroresorcinol, m. p. 174° to 179—180°, is obtained

together with oxalic acid by the oxidation of quebracho extract by nitric acid (D 1·4). The *monopotassium* salt, ($+H_2O$), pale yellow, lustrous prisms and the *dipotassium* compound, ($+H_2O$), orange needles united to moss-like aggregates, are obtained by the regulated addition of alcoholic potassium acetate solution to 2 : 4 : 6-trinitroresorcinol dissolved in alcohol; both salts explode violently when heated. The *monosodium* compound was isolated as the trihydrate, lustrous needles, and the dihydrate; it explodes with violence at 120—130°. *Disodium styphnate trihydrate* forms pale yellow, crystalline aggregates. H. W.

Polycyclic Phenols from Sodium Phenoxide Fusions. FRITZ HOFMANN and MYRON HEYN (*Brennstoff-Chem.*, 1921, **2**, 147—150).—Four of the six possible isomerides of dihydroxydiphenyl have been obtained by the fusion and partial distillation of sodium phenoxide in a stream of hydrogen or nitrogen. The gases given off at 485—490° consisted mainly of hydrogen with a little methane or ethane, but contained neither carbon dioxide nor monoxide. The distillate, about 4% of the original fused mass by weight, consisted mainly of benzene together with appreciable quantities of diphenyl and diphenyl oxide. By suitable treatment of the residue, small quantities of 2-hydroxydiphenyl, $OH{\cdot}C_6H_4Ph$, were obtained, together with much larger quantities of 2 : 2′-dihydroxydiphenyl, m. p. 109°. A new dihydroxydiphenyl, m. p. 92—93°, not previously described, was also isolated, possibly 2 : 3′-dihydroxydiphenyl. Appreciable quantities of 3 : 3′-dihydroxydiphenyl, m. p. 123·5°, and 3 : 4′-dihydroxydiphenyl, m. p. 190°, were also obtained (compare Fischer and Ehrhardt, this vol., i, 412). W. P.

Synthetic and Natural Humic Acids. WILHELM ELLER (*Brennstoff-Chem.*, 1921, **2**, 129—133. Compare A., 1920, i, 733).—Further analyses of the humic acids obtained from catechol, quinol, and *p*-benzoquinone have given concordant results agreeing with the formula $C_6H_4O_3$, previously obtained. The author suggests the annexed formula for the product.



A qualitative comparison made between the synthetic and natural humic acids gave closely agreeing results. W. P.

Optical Activation by Catalysis of Phenylmethylcarbinol. HENRI WUYTS (*Bull. Soc. chim. Belg.*, 1921, **30**, 30—41).—Phenylmethylcarbinol was subjected to catalytic dehydration by the action of 1% or more of camphorsulphonic acid at 100—108°. The predominating reaction under these conditions was the formation of the ether oxide, b. p. 156·5°/17 m., D_4^{15} 1·0058, and water, but styrene was also formed, which, however, being the most volatile substance present, could be for the most part distilled off during the operation by the employment of a suitable vacuum. At the end of the heating the active camphorsulphonic acid was

eliminated as a residue by adding the requisite quantity of benzidine and removing the unchanged carbinol and the ether oxide by distillation in a high vacuum. It was found that this distillate exhibited optical activity, but the result of successive operations on the same material showed that this activation tended towards a limit of the order of $\alpha=2{\cdot}86°$. By fractional distillation of a preparation which had only been exposed for a short period to the action of the catalyst, the unchanged carbinol and its ether oxide were isolated. Both were lævorotatory, $\alpha_D -0{\cdot}19°$ and $-1{\cdot}11°$ respectively, and there is accordingly a change of sign of rotatory power in passing from carbinol to oxide. G. F. M.

Cholesterol. XXXI. The Differing Behaviour of certain Stereoisomeric Derivatives of Cholesterol. A. WINDAUS and A. VON STADEN (*Ber.*, 1921, **54**, [*B*], 1059—1066).—The diverse behaviour of α- and β-4-chlorocholestan-7-one and their derivatives has been examined.

The structural identity of the parent substances is established in the following manner. Each is convertible into heterocholestanone (Windaus and Dalmer, A., 1919, **1**, 204), and therefore contains the oxygen atom in position 7. Further, α- and β-chlorocholestanones are convertible by fuming nitric acid into isomeric chlorodicarboxylic acids, $C_{27}H_{45}O_4Cl$; the β-acid (Windaus and Stein, A., 1904, **1**, 1010) is converted through the corresponding hydroxy-acid into the keto-acid and thence by Clemmensen's method into the acid, $CH_2<\begin{matrix}CH_2{\cdot}C_{20}H_{35}{\cdot}CO_2H\\CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO_2H\end{matrix}$, m. p. 273°, (anhydride, m. p. 118°), which has been obtained previously by Windaus and Dalmer (*loc. cit.*) from heterocholestanone. This acid and also the keto-acid mentioned above are also obtained from the *α-chloro-dicarboxylic acid*, long needles, m. p. 263—264° (*anhydride*, plates, m. p. 124°), which for this purpose is transformed into the *α-hydroxy-acid*, leaflets, m. p. 218°. It is thus proved that the chlorine atom of each of the parent substances is attached to the carbon atom in position 4. The established constitution of the final reduction product (Windaus, A., 1920, i, 434) proves that fission occurs between the carbon atoms 7 and 8.

α-Chlorocholestanone can be boiled for many hours with zinc dust and glacial acetic acid without undergoing change, at any rate as far as the replacement of chlorine by hydrogen is concerned; under similar conditions, the β-compound yields heterocholestanone. Similarly, the α-chlorodicarboxylic acid is unaffected by zinc and boiling acetic acid, whereas the β-isomeride is converted into the *acid*, m. p. 212°, having the constitution $CH_2<\begin{matrix}CH_2{\cdot}C_{20}H_{35}{\cdot}CO_2H\\CH_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH\end{matrix}$ or $CH_2<\begin{matrix}CH_2{\cdot}C_{20}H_{35}{\cdot}CH_2{\cdot}OH\\CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO_2H\end{matrix}$, or its *lactone*, colourless needles, m. p. 118°. *N*/2-Potassium hydroxide solution at 50° rapidly causes replacement of the chlorine atom by the hydroxyl group in the β-chlorodicarboxylic acid; under similar conditions, the α-chloro-compound is unaffected, protracted treatment with 25% alkali at

100° being necessary in this case to produce the like change. In replacement reactions, therefore, the halogen atom of the β-compound is much more mobile than that in the α-substance. The reverse is true in such changes as involve the elimination of hydrogen chloride; thus, α-chlorocholestanone, when distilled under diminished pressure, gives a halogen-free product (? heterocholestanone), whereas the β-derivative passes over unchanged. Similarly, the α-compound loses hydrogen chloride under the influence of alcoholic potassium hydroxide solution, whereas the β-isomeride is unaffected. H. W.

Solubility. V. Solubility of Salts of Aromatic Acids and their Ammines. FRITZ EPHRAIM (*Ber.*, 1921, **54**, [*B*], 965—973).—In continuation of previous work (this vol., i, 339, ii, 305, 338, 339), the solubility of the salts of aromatic sulphonic acids with metals of small volume (Ni, Co, Cu, Cd, Zn) has been examined; its dependence on the constitution is thus expressed. (i) The salts of all sulphonic acids which contain a chlorine or bromine atom or a nitro-group in any position in the molecule yield very sparingly soluble ammines; the ammonia-free salts are in every case more freely soluble than the ammines. (ii) All sulphonic acid which do not contain these substituents, even those which have an acidic residue other than Cl, Br, or NO_2, such as $-OH$, $-CO_2H$, or a second $-SO_3H$ group, give very freely soluble ammines; in every case the latter are more freely soluble than the ammonia-free salts (*o*-xylene-4-sulphonic acid is an exception to this rule). The preparation of the ammines of class (i) is simply effected by treating the sulphonic acid with an ammoniacal solution of a nickel salt, when a precipitate is formed immediately or after a short interval, according to the concentration of the solutions. The solubility of the ammines of different metals generally increases in the order, Ni$<$Cu$<$Cd$<$Zn; this is also the order of decreasing stability in the attachment of ammonia to metal. The ammonia-free salts of these acids are, in general, freely soluble; the metallic atom is united to water of crystallisation, and the whole molecule is therefore water-like and miscible with water.

The rules (i) and (ii) can be utilised in the purification of substituted monosulphonic acids from portions remaining unattacked and for the separation of mono- and di-sulphonic acids from one another. A single precipitation with an ammoniacal nickel solution suffices to cause the separation of the substituted monosulphonic acid as ammine whilst the other components remain in solution.

With salts of carboxylic acids, the inverse relationship is frequently encountered, the ammonia-free salts containing Cl, Br, etc., being generally less soluble than the ammines. In them, the metal is also related to $-Cl$, $-Br$, or the $-NO_2$ groups, and therefore limited in its power of union with water in virtue of its subsidiary valencies.

The behaviour of tervalent cobalt has also been investigated, and an excellent precipitant has been found in the hexamminecobalti-ion $[Co(NH_3)_6]^{\cdot\cdot\cdot}$. It reacts with formation of precipitates

in all those cases in which a sparingly soluble ammine of a bivalent metal is produced, and also in many others. The cobaltammines of lower valency have only moderate precipitating power; the salts of the *trans*-dinitritotetramminecobalti-ion, $[Co(NO_2)_2(NH_3)_4]^{\cdot\cdot}$ do not even yield precipitates with those acids which generally yield the least soluble salts. The sole exception is found in a derivative of naphthalene-β-sulphonic acid (this acid appears to show a general exceptional behaviour in its ability to form beautifully crystalline, sparingly soluble salts with heavy metals which have not been described previously. Naphthalene-α-sulphonic acid, on the other hand, behaves normally).

The behaviour of the following acids towards the chlorides of nickel, copper, cadmium, and zinc and their ammines, and towards hexamminecobalti-chloride and chloropentamminecobalti-chloride is fully described: 5-nitro-6-nitro- and -7-nitronaphthalene-α-sulphonic acids, 2 : 6-dinitro-*m*-xylene-4-sulphonic acid, 2 : 6-dinitrotoluene-4-sulphonic acid, 4 : 5-dichloro-2-nitrobenzenesulphonic acid, 2 : 5-dichlorobenzenesulphonic acid, 5-chloronaphthalene-α-sulphonic acid, 3 : 4-dichlorobenzenesulphonic acid, 4-chloro-2-nitrobenzenesulphonic acid, 2-chloro-3 : 5-dinitrobenzenesulphonic acid, *m*-nitrotoluene-4-sulphonic acid, *p*-nitrotoluene-2-sulphonic acid, dibromonaphthalene-β-sulphonic acid. Each individual of this group gives precipitates with hexamminecobalti-chloride and with the ammines of bivalent metals; with the nickel ammines, the separation is so complete that it is almost possible to base a method of estimation on it. The following acids of class (ii) have been examined: *m*-xylene-4-sulphonic acid, benzenesulphonic acid, *m*-sulphobenzoic acid, *p*-sulphobenzoic acid, *m*-xylene-5-sulphonic acid, *o*-xylene-4-sulphonic acid, naphthalene-α- and -β-sulphonic acids, 6-hydroxynaphthalene-β-sulphonic acid, 1-hydroxynaphthalene-5-sulphonic acid, α-naphthol-5-sulphonic acid, phenol-*p*-sulphonic acid.

None of the di- or tri-sulphonic acids, even if a Cl, Br, or NO_2 group is present, gives a precipitate with ammoniacal nickel, copper, cadmium, or zinc solutions (or with the corresponding ammonia-free solutions) or with carbonatotetrammine- or purpureo-cobalt salts. Hexamminecobalti-chloride yields precipitates with 1-nitronaphthalene-3 : 7-disulphonic acid, 1-nitronaphthalene-3 : 6-disulphonic acid, β-bromonaphthalenedisulphonic acid, naphthalene-1 : 6-disulphonic acid, naphthalene-1 : 5-disulphonic acid, naphthalene-2 : 7-disulphonic acid, 2 : 6-dinitrobenzene-1 : 4-disulphonic acid, β-naphthol-6 : 8-disulphonic acid (but not with benzene-*m*-disulphonic acid, β-naphthol-3 : 6-disulphonic acid, and 3 : 5-disulphobenzoic acid), with 7-chloronaphthalene-1 : 3 : 6-trisulphonic acid, 5-nitronaphthalene-1 : 3 : 7-trisulphonic acid (but not with naphthalene-1 : 3 : 6-trisulphonic acid or 7-chloronaphthalene-1 : 3 : 6-trisulphonic acid). H. W.

Thioamides. I. Preparation of Thioamides with the Aid of Aluminium Sulphide. Karl Kindler and Friedrich Finndorf (*Ber.*, 1921, **54**, [*B*], 1079—1081).—Thioamides are

prepared in good and sometimes quantitative yield by heating the requisite acid amide with aluminium sulphide and a substance containing water of crystallisation such as sodium sulphate hexahydrate in a sealed tube; the quantities of materials are so chosen that an excess of hydrogen sulphide is formed. Alternatively, the ammonium salt of the requisite acid may be employed, in which case the presence of a hydrate is unnecessary. The preparation of thiobenzamide from benzamide and acetamide from ammonium acetate is described in detail. H. W.

Thioamides. II. Reduction of Thioamides to Primary Amines. KARL KINDLER and WALTER DEHN (*Ber.*, 1921, **54**, [*B*], 1080—1081).—Thioamides give good yields of the corresponding primary amines when reduced by aluminium amalgam in neutral solution. The conversion of thiobenzamide into benzylamine and of thioacetamide into ethylamine in aqueous alcoholic solution is described. H. W.

The Acid Constituents of the Resin of the Maritime Pine. GEORGES DUPONT (*Compt. rend.*, 1921, **172**, 1184—1186. Compare this vol., i, 487).—Pimaric acid as isolated from pine resin and purified by Vesterberg's method consists of a mixture of 37% of the dextro-acid and 63% of the lævo-acid. W. G.

The Acid Constituents of the Resin of the Maritime Pine. Isomerisation of the Pimaric Acids. GEORGES DUPONT (*Compt. rend.*, 1921, **172**, 1373—1375. Compare preceding abstract). —*l*-Pimaric is slowly isomerised by heat; acetic acid and more particularly hydrochloric acid exert a marked catalytic effect on this change. Using hydrochloric acid as a catalyst, it was possible to show that the change takes place in two stages. In the first stage, *α-pimarabietic acid*, $[\alpha]_J -76{\cdot}4°$, is formed, and then in the second stage is converted into β-pimarabietic acid, m. p. 172—173°, $[\alpha]_J -100{\cdot}1°$ (compare Schultz, *Mon. Sci.*, 1920, **10**, 102). *d*-Pimaric acid does not undergo isomerisation under these conditions. W. G.

5-Iodo-3-nitro-4-hydroxybenzoic Acid and the Mercury Derivative of *m*-Nitro-*p*-hydroxyphenylcarbinol. MORRIS S. KHARASCH (*J. Amer. Chem. Soc.*, 1921, **43**, 1203—1205).—The constitution assigned to the mercury derivative of *m*-nitro-*p*-hydroxyphenylcarbinol by Hart and Hirschfelder (this vol., i, 140) is shown to be incorrect. The mercury is actually in position 5, that is ortho to the hydroxyl group. When treated with iodine in potassium iodide this mercury derivative yields 5-*iodo*-3-*nitro*-4-*hydroxyphenylcarbinol*, m. p. 138°, which when oxidised with potassium permanganate in alkaline solution gives 5-iodo-3-nitro-4-hydroxybenzoic acid, also prepared by direct nitration of 5-iodo-4-hydroxybenzoic acid. W. G.

Preparation of Aurothiosalicylic [*o*-Aurothiolbenzoic] Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 157226; from *Chem. Zentr.*, 1921, ii, 962).—*o*-Thiolbenzoic acid is

treated with a gold haloid double salt. For example, solutions of *o*-thiolbenzoic acid and potassium aurobromide in ethyl acetate are mixed and after filtration, o-*aurothiolbenzoic acid*, $SAu\cdot C_6H_4\cdot CO_2H$, is precipitated by absolute ethyl alcohol as a yellow powder. It gives alkali salts soluble in water and has medicinal properties. The *potassium* salt, obtained by dissolving the acid in a dilute aqueous solution of potassium hydroxide, is obtained as a white powder by precipitation with ethyl alcohol. G. W. R.

Resolution of Racemic Acids by Optically Active Alcohols. II. The Resolution of Atrolactic and α-Hydroxy-β-phenylpropionic Acids by *l*-Menthol. HENRY WREN and EDWARD WRIGHT (Trans., 1921, **119**, 798—803).

Specific Rotation of the Active Sodium Salts of γ-Hydroxyphenylbutyric Acid and the [Asymmetric] Reduction of Benzoylpropionic Acid in the Body. H. THIERFELDER and ERICH SCHEMPP (*Zeitsch. physiol. Chem.*, 1921, **114**, 94—100).—The sodium salt of the hydroxy-acid from human and dog's urine (after administration of the keto-acid) has $[\alpha]_D$ $-12{\cdot}8°$ to $-13{\cdot}1°$. γ-Hydroxyphenylbutyric acid has now been resolved by means of brucine, and furnishes two sodium salts with rotations approximately $+3°$ and $-13°$, so that the reductions by the animal organism, unlike that by yeast, leads to the formation of one enantiomorph only. C. R. H.

Reduction of Fluoreneglyoxylic Ester. WILHELM WISLICENUS and HERBERT WEITEMEYER (*Ber.*, 1921, **54**, [*B*], 978—979. Compare Sieglitz, this vol., i, 110).—Ethyl fluoreneoxalate is slowly reduced by aluminium amalgam in the presence of moist ether to *ethyl fluorene-9-hydroxyacetate* [*fluoren-9-glycollate*]

$$C_{13}H_9\cdot CH(OH)\cdot CO_2Et,$$

colourless, interwoven needles, m. p. 84°. The latter is converted by the calculated quantity of alcoholic sodium hydroxide solution mainly into *benzofulvene-ω-carboxylic acid*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C{:}CH\cdot CO_2H$, slender, yellow needles, m. p. 222—223°, small amounts of fluoreneglycollic acid appearing to be formed simultaneously. H. W.

The Solubility of Phthalic Acid in Water and in Sodium Sulphate Solutions. L. McMASTER, E. BENDER, and E. WEIL (*J. Amer. Chem. Soc.*, 1921, **43**, 1205—1207).—The solubility of phthalic acid in water and in 10% and 15% solutions of sodium sulphate respectively is given over the temperature range 25—85°. The solubility diminishes slightly as the concentration of the sodium sulphate increases. W. G.

Preparation of Phthalic Anhydride. HIDEMATSU SASA (Brit. Pat. 140051).—Phthalic anhydride is obtained by adding 35 kilos. of α-nitronaphthalene to 450 kilos. of concentrated sulphuric acid (D 1·82) heated at 150—160°, and when the former has melted, 80—90 kilos. of iron borings or other reducing metal are stirred

in. After the vigorous evolution of gas has subsided, the phthalic anhydride is distilled off in a suitable vacuum at about 300°.

G. F. M.

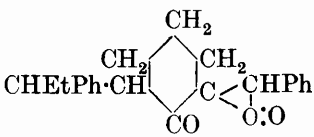
New Components of Colophony, the Colophenic Acids and their Analogues. OSSIAN ASCHAN (*Ber.*, 1921, **54**, [*B*], 867—886).—A new series of acids has been isolated from the residues left after the isolation of pinabietic acid from the "black liquor" of the sulphate cellulose factories (compare A., 1919, i, 326) and also from American and Finnish colophony. The acids have the general formula $C_nH_{2n-10}O_4$, and are provisionally named in accordance with the number of carbon atoms present in the molecule, hexadecacolophenic acid thus having the formula $C_{16}H_{22}O_4$. They are distinguished from the resin acids by their monobasic nature, although four oxygen atoms are present in the molecule. One of the two remaining oxygen atoms is present in the hydroxyl group; the aldehyde radicle is not present, and ketonic characteristics could not be established definitely. The lactone ring is absent. The acids themselves are colourless or pale yellow, but the solutions of their alkali salts are dark yellow to brownish-yellow. In contrast to those of the resin acids, the sodium salts of the colophenic acids are freely soluble in cold water and the solutions are unaffected by carbon dioxide. The barium, calcium, silver, and copper salts are comparatively freely soluble in water. The acids are highly unsaturated and immediately decolorise permanganate. The colour reactions with nitric acid, sulphuric acid, and Mach's reagent are described.

The isolation of hexadecacolophenic acid from the mother liquors obtained in the preparation of pinabietic acid is effected by separating the remainder of the latter (as sodium salt) by addition of sodium chloride, removal of resinates by treatment of the filtrate with carbon dioxide, precipitation of the colophenic acid, and purification by repetition of the process. The preparation of the acids from colophony is effected (1) by solution of the latter in hot aqueous sodium carbonate, treatment of the cold solution with carbon dioxide until precipitation of the acid resinate is complete and acidification of the filtrate or (2) by solution in sodium hydroxide followed by successive treatments with sodium chloride and carbon dioxide and then by precipitation. The further purification of the crude acids is effected by taking advantage of the fact that the colophenic acids are soluble in benzene but insoluble or nearly so in light petroleum, by which they are precipitated from solution in benzene. The following individual acids are described. *Hexadecacolophenic acid*, $C_{16}H_{22}O_4$, from the mother-liquors of the preparation of pinabietic acid, large, yellow granules, m. p. 96—105°, or almost colourless powder, m. p. 86—98°, $[\alpha]_D^{17}$ +22·33° or +21·66° (for different specimens), in benzene solution (the *silver* salt and *acetyl* derivative were analysed). The acid appears to be stable towards molten potassium hydroxide. It was also isolated (m. p. 115—123°, $[\alpha]_D$ +28·8° in benzene solution) from two varieties of technical American colophony, but it does not

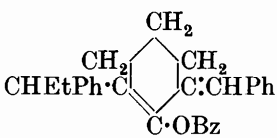
appear to be present in all sorts. It was prepared artificially by the action of hydrogen peroxide on a slightly alkaline solution of pinabietic acid: $C_{15}H_{19}MePr^{\beta}\cdot CO_2H + 2H_2O = C_3H_8 + CH_4 + C_{15}H_{19}(OH)_2\cdot CO_2H$. *Heptadecacolophenic acid*, $C_{17}H_{24}O_4$, m. p. 100—105° after softening at 70—75°, was obtained from Finnish colophony, and closely resembled the lower homologue. *Octadecacolophenic acid* was isolated from American colophony. *Eïcosicolophenic acid*, obtained from two dark brown technical specimens of American colophony, is molten below 110° after softening at 80—90°. H. W.

Use of Aluminium Chloride and Ferric Chloride in the Preparation of Phenolphthalein. CHARLES FREDERICK WARD (Trans., 1921, **119**, 850—852).

Action of Magnesium Ethyl Bromide on 1 : 3-Dibenzylidene-2-*cyclo*hexanone and 1 : 3-Dibenzylidene-4-methyl-2-*cyclo*hexanone. MANOLESCO (*Compt. rend.*, 1921, **172**, 1360—1362).—When 1 : 3-dibenzylidene-2-*cyclo*hexanone is slowly added to an ethereal solution of magnesium ethyl bromide, a considerable quantity of oily material is formed, together with a crystalline *compound*, $C_{22}H_{24}O_3$, m. p. 137·05°, which is a peroxide having the constitution of the annexed formula.



When reduced by potassium iodide and acetic acid, it loses one atom of oxygen, giving apparently the *oxide*, $C_{22}H_{24}O_2$, m. p. 111°. The peroxide condenses with benzoyl chloride to give a *benzoyl* derivative (annexed formula), m. p. 105°; and with cinnamoyl chloride to give a *cinnamoyl* derivative, m. p. 122—123°.



Dibenzylidene-γ-methyl*cyclo*hexanone similarly condenses with magnesium ethyl bromide, giving a *peroxide*, $C_{23}H_{26}O_3$, m. p. 119—120°. W. G.

Piperitone. I. The Occurrence, Isolation, and Characterisation of Piperitone. JOHN READ and HENRY GEORGE SMITH (Trans., 1921, **119**, 779—789).

Diaminoanthraquinones. M. BATTEGAY and J. CLAUDIN (*Bull. Soc. Ind. Mulhouse*, 1921, **87**, 71—72).—When 1 : 3-dibromoanthraquinone (this vol., i, 349) is treated in nitrobenzene solution with *p*-toluenesulphonamide, potassium carbonate, and powdered copper, 1 : 3-*ditolylsulphonylaminoanthraquinone*,

$$C_{14}H_6O_2(NH\cdot SO_2\cdot C_6H_4Me)_2,$$

m. p. 245°, is obtained. This dissolves in cold 96% sulphuric acid with an orange-red colour, and when this solution is heated on the water-bath for one hour and then poured into aqueous ammonia, brick-red flakes of 1 : 3-diaminoanthraquinone are precipitated. This can be crystallised from nitrobenzene as red crystals having a black reflex and m. p. 290°. The dibenzoyl derivative has

m. p. >300° and, although insoluble in alcohol and only slightly soluble in other usual solvents, can be obtained as brown crystals from nitrobenzene. It dissolves in cold concentrated sulphuric acid to give an orange coloration.

1 : 6- and 1 : 7-Diaminoanthraquinones were obtained by treatment of the corresponding nitroanthraquinonesulphonic acids with ammonia under pressure. Both were crystallised from anisole.

1 : 6-*Diaminoanthraquinone* forms red spangles, m. p. 292°, and the diacetyl and dibenzoyl derivatives have m. p. 295° and 275° respectively. The latter substance dissolves in cold concentrated sulphuric acid with a red colour.

1 : 7-Diaminoanthraquinone forms red needles, m. p. 290°, and the m. p. of the diacetyl and dibenzoyl derivatives are 283° and 325° respectively. The latter substance dissolves in cold concentrated sulphuric acid to give an orange colour.

Both the 1 : 6- and 1 : 7-diaminoanthraquinones are easily transformed into the corresponding dihydroxyanthraquinones by diazotisation and boiling with water. A. J. H.

Studies in the Camphane Series. XXXIX. *p*-Aminophenylaminocamphor (Camphoryl-*p*-phenylenediamine). MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (Trans., 1921, **119**, 789—798).

Furfurylidenecamphor and some of its Derivatives. (MLLE) WOLFF (*Compt. rend.*, 1921, **172**, 1357—1360. Compare Haller and Bauer, A., 1906, i, 441; 1908, i, 357).—Furfuraldehyde condenses with sodium camphor to give *furfurylidenecamphor*, m. p. 64°; b. p. 171—175°/11 mm., which, when hydrogenated in the presence of reduced nickel, yields *tetrahydrofurfurylcamphor*, b. p. 166°/14 mm. Furfurylidenecamphor condenses with organomagnesium derivatives to give furylarylcamphorylmethanes,

$$C_8H_{14}<\begin{matrix}CH\cdot CHR\cdot C_4OH_3,\\ |\\ CO\end{matrix}$$

of which the following are described: *Phenylfurylcamphorylmethane*, m. p. 114°; *benzylfurylcamphorylmethane*, an oil; p-*tolylfurylcamphorylmethane*, b. p. 234°/17 mm.; and p-*anisylfurylcamphorylmethane*, b. p. 255°/17 mm. W. G.

The Molecular Refraction and the Specific Rotatory Power of Furfurylidenecamphor and some of its Derivatives. (MLLE) WOLFF (*Compt. rend.*, 1921, **172**, 1404—1405. Compare preceding abstract).—The following physical constants are given, the molecular refractions having been determined in toluene solutions at temperatures varying between 23·2° and 24·7°. Furfurylidenecamphor has M_α 69·62; M_β 72·28; M_D 70·23; $[\alpha]_D^{18}$ +339°; tetrahydrofurfurylcamphor has M_α 66·58; M_β 68·24; M_D 66·82; $[\alpha]_D^{20}$ +42°; phenylfurylcamphorylmethane has M_α 89·46; M_β 91·50; M_D 90·16; $[\alpha]_D^{20}$ +66°; benzylfurylcamphorylmethane has M_α 93·94; M_β 96·23; M_D 94·50; $[\alpha]_D^{18}$ +57°; tolylfurylcamphorylmethane has M_α 94·82; M_β 97·20; M_D 95·51; $[\alpha]_D^{24}$ +59°; anisylfurylcamphorylmethane has M_α 96·09; M^β 98·82; M_D 96·80; $[\alpha]_D^{24}$ +66°. W. G.

The Volatile Oil from the Leaves of the "Wild Pimento" of Jamaica. O. D. ROBERTS (*J. Soc. Chem. Ind.*, 1921, **40**, $94—96_T$).—The composition of the volatile oil from the leaves of *Amomis jamaicensis* is approximately as follows: Terpenes, including α-phellandrene and dipentene, 17·0%; cineole, 15·0%; aldehydes, unidentified, 0·1%; alcohols, chiefly *l*-linalool with some geraniol, 38·3%; esters, as linalyl acetate, 1·5%; phenols, unidentified, 0·1%; acids, acetic and hexoic in the free state, 0·2%; residue, probably containing sesquiterpenes, 27·8%. W. G.

Essential Oil from the Leaves of *Skimmia Laureola*. JOHN LIONEL SIMONSEN (*J. Soc. Chem. Ind.*, 1921, **40**, 126—127).—The oil, which was pale emerald green in colour and had D_{30}^{30} 0·9041, n_D^{30} 1·4648, acid value 3·63, saponification value 197·96, saponification value after acetylation 238·6, was prepared by distilling the shade-dried leaves in steam, the yield being about 0·5% of the weight of the dried leaves. It consists mainly of *l*-linalyl acetate, whilst, in addition, a hydrocarbon, b. p. 130—135°/200 mm., 176—182°/695 mm., D_{30}^{30} 0·859, n_D^{30} 1·471, $[\alpha]_D^{30}$ −4·11°, which could not be further identified, *l*-linalool and a complex mixture of sesquiterpene alcohols and esters were isolated. H. W.

Preparation of Amino-compounds of Cinchona Alkaloids and their Derivatives. C. F. BOEHRINGER & SOEHNE (D.R.-P. 335113; from *Chem. Zentr.*, 1921, ii, 963).—Cinchona alkaloids which contain a free phenol hydroxyl group are coupled with diazonium salts, the azo-compounds thus obtained reduced by the usual methods, and the resulting amino-derivatives of the alkaloids alkylated on the phenol hydroxyl groups. *Aminoethylhydroquinine* obtained from hydrocupreineazobenzenesulphonic acid by way of aminohydrocupreine corresponds with the amino-compound obtained by reduction of nitroethylhydrocupreine (D.R.-P. 283537). *Cupreineazobenzenesulphonic acid* is obtained from cupreine and *p*-diazobenzenesulphonic acid in alkaline solution; the *sodium* salt crystallises in hexagonal tables with 6 molecules of water; the free acid crystallises in red, prismatic tables with 3 molecules of water of the composition $C_{25}H_{26}O_5N_4S$; m. p. 257° (decomp.). *Aminocupreine*, $C_{19}H_{23}O_2N_3$, is obtained by reduction of cupreineazobenzenesulphonic acid by sodium hydrogen sulphite in alkaline solution, and forms yellow crystals, m. p. 195 (decomp.), unstable like *o*-aminophenol, and forms four series of salts; gives by catalytic reduction *aminohydrocupreine*. The latter gives, with ethyl sulphate in alkaline solution, *aminoethylquinine*, $C_{21}H_{27}O_2N_3$, which forms rectangular, prismatic needles or tables like cholesterol; m. p. 213—214°. The monosulphate is almost colourless and the disulphate red. By catalytic reduction, *aminoethylhydroquinine* is obtained. G. W. R.

Interconversion of Creatine and Creatinine. I and II. AMANDUS HAHN and GEORG BARKAN (*Zeitsch. Biol.*, 1920, **72**, 25—36, 305—313).—When kept for one or two weeks at ordinary temperatures in $N/10$ to N-sodium hydroxide, creatinine is mostly

transformed into creatine, and an equilibrium is attained, which can also be reached from the other side. k=[creatine]/[creatinine]= 2·12, and is not affected by the changes in the concentrations of the alkali employed. The reaction is unimolecular and slightly complicated by a side reaction resulting in the formation of traces of an amine. In acid solution, the change from creatine to creatinine is complete, because the latter is much the stronger base. At ordinary temperatures in N/10-hydrochloric acid, the change requires about a fortnight. The authors have determined the hydrolytic dissociation of the chlorides electrometrically, and hence calculate the dissociation constants at 17° : $6{\cdot}14\times10^{-12}$ and $1{\cdot}85\times10^{-10}$, for creatine and creatinine respectively. [Wood, Trans., 1903, **83**, 576, found at 40° $1{\cdot}81\times10^{-11}$ and $3{\cdot}5\times10^{-11}$ respectively.] In the second paper, it is shown that creatinine, when added to acid urine, is not changed, but when 0·1—0·6% of creatine is added to urine, it is converted quantitatively into creatinine in twenty-four hours. For the estimation of creatine in urine, the authors mix the latter with an equal volume of $2N$-HCl and heat for twenty-four hours at 60°, instead of a shorter time at 100°. G. B.

A New Degradation Product of Physostigmine [Eserine]. EDGAR STEDMAN (Trans., 1921, **119**, 891—894).

Mitragynine and Mitraversine, Two New Alkaloids from Species of Mitragyne. ELLEN FIELD (Trans., 1921, **119**, 887—891).

New Sulphonated Derivatives of Osindole and Isatin. J. MARTINET and O. DORNIER (*Compt. rend.*, 1921, **172**, 1415—1417).—When phenylacetic acid is warmed on a water-bath for one hour with sulphuric acid and the product is nitrated, o-*nitro*-p-*sulphophenylacetic acid* is obtained, giving an unstable *silver* salt. If the acid in solution is warmed with sodium sulphide, *sodium oxindole*-6-*sulphonate* is obtained, from which the free *acid* is readily liberated. The latter gives an *oxime*, which, when reduced with stannous chloride, gives *amino-oxindole*-6-*sulphonic acid* as its stannichloride. The latter, when treated in boiling aqueous suspension with copper acetate, gives *isatin*-6-*sulphonic acid* isolated as its *potassium* or *barium* salts. The potassium salt, when condensed with indoxyl in acetic acid solution, gives an indirubin which dyes animal fibres violet. The sodium salts of oxindole-6-sulphonic acid and isatin-6-sulphonic acid condense together to give *sodium* iso*indigotin*-6 : 6′-*disulphonate*. W. G.

Action of Chloraloxime on Aromatic Amines; Synthesis of Isatins. TH. MARTINET and P. COISSET (*Compt. rend.*, 1921, **172**, 1234—1236).—Chloraloxime condenses with aniline in neutral solution to give oximinoethenyldiphenylamidine,

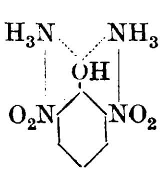
NPh:C(NHPh)·CH:N·OH,

but in acid solution it gives oximinoacetanilide, NHPh·CO·CH:N·OH. The latter substance, when warmed with sulphuric acid, yields isatin. In a similar way, starting with p-chloro-o-anisidine hydrochloride in place of aniline, the authors have prepared *oximinoaceto*-5-*chloro*-o-*anisidide*, $OMe{\cdot}C_6H_3Cl{\cdot}NH{\cdot}CO{\cdot}CH{:}N{\cdot}OH$, m. p.

190°, and 4-*chloro-7-methoxyisatin*, m. p. 255°, giving a *phenylhydrazone*, m. p. 245°, and an *oxime*, m. p. 230°; a *barium isatate*, $(C_9H_7O_4NCl)_2Ba,2H_2O$, and a *copper* salt were also prepared from it. When condensed with indoxyl the isatin gives 4-*chloro-7-methoxyindirubin*. W. G.

Preparation of 3-Nitroquinoline and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 335197; from *Chem. Zentr.*, 1921, ii, 962).—*o*-Amino-derivatives of aromatic aldehydes or ketones or derivatives of these aldehydes or ketones are condensed with methazonic acid. 3-*Nitroquinoline* is obtained from *o*-aminobenzaldehyde and methazonic acid solution after remaining for several hours at ordinary temperatures, and acidifying with hydrochloric acid; it forms colourless crystals, m. p. 128°, easily volatile in steam. By the action of methazonic acid on an alkaline solution of isatin and acidifying with hydrochloric acid, β-isatinoxime is obtained together with 3-*nitroquinoline-4-carboxylic* acid, which can be separated from the oxime by means of sodium hydrogen carbonate and forms colourless needles, m. p. 204°. By treating *o*-aminoacetophenone, dissolved in water with the addition of hydrochloric acid, with methazonic acid solution and acidifying with hydrochloric acid, a mixture is obtained of *o*-aminoacetophenoneoxime and 3-*nitro-4-methylquinoline*. These are separated by treatment with sodium hydroxide solution, in which only the oxime is soluble. The nitro-compound crystallises from hot water in colourless prisms, m. p. 118°, volatile in steam. G. W. R.

Reduction of certain Aromatic Nitro-compounds by Ammonium Sulphide. A. KORCZYŃSKI and S. PIASECKI (*Anzeiger Akad. Wiss. Krakau*, 1917, 176—183; from *Chem. Zentr.*, 1921, i, 866—867).—The reduction of *s*-trinitrobenzene is influenced by the nature of the solvent used. Using as solvent water or weaker alcohol than described by Bader (A., 1891, 1030), 5-nitro-*m*-phenylenediamine is obtained instead of dinitroaniline. The reaction shows a close connexion with the formation of the additive product of *s*-trinitrobenzene with two molecules of ammonia described by Korczyński (A., 1908, i, 977; 1909, i, 639), which is also formed as an intermediate product in the reduction with ammonium sulphide. As in the reduction of 2:4:6-trinitrophenol, 4-nitro-2:6-diaminophenol is formed; the groups reduced are those which exert the greatest influence on the formation of the abnormal salt (compare Korczyński, *loc. cit.*). Also in the partial reduction of 2:4-dinitrobenzoic acid the first nitro-group to be reduced is the one in the para-position, which has the greatest influence in the formation of the abnormal salt, and not the one next to the acid group, as hitherto supposed. In aqueous solution, both groups are reduced by ammonium sulphide. The connexion between the formation of an abnormal salt and capability of reduction is explained by postulating (annexed formula) a mutual satisfaction of residual affinities between the nitro-groups concerned and the groups



in the region of the activity of the acid hydrogen; in other words, the ammonia molecules.

5-*Nitro*-m-*phenylenediamine*, obtained by gradual addition of concentrated aqueous ammonium sulphide solution to a boiling aqueous solution of *s*-trinitrobenzene, crystallises in brownish-red needles, m. p. 159°. The *dibromo*-derivative forms brownish-yellow scales, m. p. 183—184°. The *acetyl* derivative is almost insoluble. 5-*Nitro*-1 : 3-*di-trinitroanilinobenzene* is formed by heating 5-nitro-*m*-phenylenediamine with 2 molecules of picryl chloride and the calculated amount of sodium acetate under a reflux condenser; it forms orange-red crystals, blackens at 240°, m. p. 260° (decomp.). *Nitrochrysoidine*, $NPh{:}N{\cdot}C_6H_2(NH_2)_2{\cdot}NO_2$, is obtained in the form of the hydrochloride by gradual addition of a diazotised solution of aniline in dilute hydrochloric acid to a solution of nitrophenylenediamine in 10% hydrochloric acid and addition of potassium acetate solution until the hydrochloric acid reaction nearly disappears; it forms brown crystals with steely lustre; the aqueous solution is orange coloured and turns red on adding excess of hydrochloric acid. 1-*Nitro*-3-*amino*-6-*dimethylaminophenazine*,

$$NMe_2{\cdot}C_{12}N_2H_5(NH_2){\cdot}NO_2,$$

is formed by heating for three hours an aqueous solution of the crystalline product obtained by warming together for a short time nitrosodimethylaniline hydrochloride and nitro-*m*-phenylenediamine; it forms reddish-brown needles with varying amounts of water of crystallisation; it gives red solutions in dilute and blue solutions in concentrated acids. Anhydro-compounds of varying composition are obtained by condensation of nitro-*m*-phenylenediamine with formaldehyde in aqueous solution. 4-Nitro-2 : 6-diaminophenol is obtained by passing hydrogen sulphide into a hot solution of picric acid in dilute ammonia until no precipitate is given by addition of dilute hydrochloric acid to a small quantity of the filtered concentrated solution; the solution is evaporated to small volume with dilute hydrochloric acid, sulphuric acid (1 : 1) is added to the filtered solution and the precipitated sulphate is decomposed by sodium acetate. 3 : 5-Diaminobenzoic acid is formed by reduction of 3 : 5-dinitrobenzoic acid in aqueous solution. The latter, by complete reduction in aqueous solution, gives *m*-phenylenediamine, and by careful partial reduction, 2-nitro-4-aminobenzoic acid. 4-*Dimethylaminobenzeneazo*-2-*nitrobenzoic acid*, $NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(NO)_2{\cdot}CO_2H$, formed by diazotisation of nitroaminobenzoic acid and heating with an alcoholic solution of dimethylaniline, crystallises in scarlet-red scales tinged with violet, m. p. 216° (decomp.), soluble in dilute acids and alkalis; the compound is a nitro-derivative of methyl-red, and is not less sensitive as an indicator. G. W. R.

The Reactions of the Formamidines. IX. The Synthesis of 5-Phenylpyrazole-4-carboxylic Acid. F. B. DAINS and W. S. LONG (*J. Amer. Chem. Soc.*, 1921, **43**, 1200—1202. Compare A., 1909, i, 781; 1916, i, 751; 1918, i, 238).—Anilinomethylene-benzoylacetanilide reacts with hydrazine sulphate in the presence

of sodium carbonate in alcohol to give 5-*phenylpyrazole*-4-*carboxylanilide,* m. p. 182°, which crystallises with one molecule of methyl or ethyl alcohol and gives an unstable *hydrochloride.* When boiled with concentrated hydrochloric acid, it is hydrolysed, yielding 5-*phenylpyrazole*-4-*carboxylic acid,* m. p. 260°, which gives *silver, copper,* and *barium* salts and an *ethyl* ester, m. p. 85—86°, which was, however, prepared indirectly. Neither the free acid nor its ester reacted with aniline.

5-*Phenylpyrazole*-4-*carboxyl*-p-*anisidide,* m. p. 161°, was obtained by the action of hydrazine on benzoyl-*p*-anisidylaminomethylene-aceto-*p*-anisidide and 5-*phenyl*-4-*pyrazolecarboxyl*-o-*anisidide,* m. p. 127°, was similarly prepared. W. G.

The Preparation and Properties of some Salts of Uric Acid. L. J. Curtman and D. Hart (*J. Biol. Chem.*, 1921, **46**, 599—613).—*Zinc urate,* $ZnC_5H_2O_3N_4,2H_2O$, was prepared by the addition of zinc acetate to an aqueous solution of monopotassium urate. The following nickel and copper salts of complex composition were similarly prepared, for which the formulæ $NiC_5H_2O_3N_4,NiCO_3,2H_2O$, $Ni(C_5H_3O_3N_4)_2,xH_2O$, $7CuC_5H_2O_3N_4$, $3CuO,4H_2O$, $5Cu(C_5H_3O_3N_4),2CuO,20H_2O$ are suggested. E. S.

The Relationship between Resinification and the Constitution of Chemical Compounds. Walther Herzog (*Oester. Chem. Zeit.*, 1921, **24**, 76—79).—The grouping –N:C:N– is characteristic of a whole class of substances which readily undergo polymerisation with the formation of resins, and may therefore be regarded as a typical resinophore group. A general method for the preparation of such synthetic resins consists in heating *s*-disubstituted thiocarbamides, or carbamides at temperatures above their melting points, either alone, or, preferably, in presence of a solvent, whereby hydrogen sulphide or water is eliminated and the resulting carbodi-imides are simultaneously converted into the resinous polymeride. For example, *s*-diphenylthiocarbamide, dissolved in an equal quantity of aniline, is converted, by heating for forty hours at the boiling point of the solution, into a resin the greater part of which can be distilled at 190—240°/30—40 mm. The distillate, representing 67% of the theoretical yield, forms a clear amber-like resin, m. p. 144°, soluble in benzene, turpentine, and fatty oils. Similar resins were prepared in like manner from di-*p*-tolylthiocarbamide, phenyl-*p*-tolylthiocarbamide, di-*p*-chlorophenylthiocarbamide, phenylallylthiocarbamide, di-α-naphthylthiocarbamide, di-*m*-4-xylylthiocarbamide, dibenzylthiocarbamide, diphenylenethiocarbamide (from carbon disulphide and benzidine), and pinacolylthiocarbamide. Mixed resins were also obtained from mixtures of the above thiocarbamides, and, unlike the simple resins, they showed no tendency to depolymerisation with deposition of the crystalline carbamide. This property should render them of value as synthetic lacs. Dehydration of the substituted carbamides resulted in the formation of resins identical with those produced from the corresponding thiocarbamides, but the reaction does not

proceed so smoothly, and the yields are accordingly diminished. A phosphorus resin containing the group –N⁚P⁚N– was prepared in a similar manner from triphenylphosphamide. G. F. M.

The Hofmann and Curtius Transformations in Relation to Steric Hindrance. H. L. Buning (*Rec. trav. chim.*, 1921, **40**, 327—353).—In order to distinguish between the effects of ortho-substituents on the different valencies of a side-chain attached to a benzene nucleus, a number of di-ortho-substituted benzamides, benzohydrazides, and benzoazides have been examined. The results seem to show that if the bonds be numbered from the nucleus, $\mathrm{R\underset{(1)}{—}CO\underset{(2)}{—}NH\underset{(3)}{—}H}$, $\mathrm{R\underset{(1)}{—}CO\underset{(2)}{—}\overset{\diagup N \diagdown}{N\underset{(3)}{—}N}}$, $\mathrm{R\underset{(1)}{—}CO\underset{(2)}{—}NH\underset{(3)}{—}NH\underset{(4)}{—}H}$, then, contrary to the steric hypothesis in its simple form the bonds (1) and (3) are weakened and the bonds (2) and (4) strengthened by the introduction of ortho-substituents.

That the bond (2) in amides is strengthened by ortho-substitution is shown, for example, by the differences in the case of hydrolysis of substituted benzamides (Trans., 1897, **71**, 229). The Hofmann transformation, on the other hand, involves the rupture of bonds (1) and (3), as does the Curtius transformation of azides. It is significant, therefore, that the amides and azides of 2 : 4 : 6-tribromobenzoic acid, 2 : 6-dibromobenzoic acid, and 3 : 5-dibromo-*p*-toluic acid undergo the Hofmann and Curtius reactions respectively more easily than benzamide and benzazide. Again, the formation of dibenzohydrazides from benzoyl chlorides and benzohydrazides involves the fission of the bonds (2) and (4) respectively of the condensing substances. In accord with the general conclusion, therefore, is the fact that the condensation of benzoyl chloride with benzohydrazide takes place more rapidly, and that of 2 : 4 : 6-tribromobenzoyl chloride with 2 : 4 : 6-tribromobenzohydrazide more slowly, under comparable experimental conditions, than the condensation either of benzoyl chloride with 2 : 4 : 6-tribromobenzohydrazide or of 2 : 4 : 6-tribromobenzoyl chloride with benzohydrazide.

The author considers that there can be no objection to thus employing intermolecular and intramolecular changes in the same inquiry, since both types of change can be brought under the same general scheme of formulation, regarding which the original paper should be consulted.

3 : 5-*Dibromo*-p-*toluoyl chloride*, m. p. 46°, is obtained from the acid by the action of phosphorus pentachloride. 2 : 4 : 6-*Tribromobenzohydrazide* (needles, m. p. 234°, decomp.), 2 : 6-*dibromobenzohydrazide* (granules or small needles, m. p. 204°), and 3 : 5-*dibromo*-p-*toluoylhydrazide* (needles, m. p. 173°) are obtained from the corresponding acid chlorides by treating with hydrazine hydrate. *α-Benzoyl-β-*2 : 4 : 6-*tribromobenzoylhydrazine* (m. p. 290—295°, decomp.) and *di*-2 : 4 : 6-*tribromobenzoylhydrazine* (decomposes 365—370°) are prepared in the manner indicated above. *Methyl* 3 : 5-*dibromo*-p-*toluate* (needles, m. p. 48°), which, like methyl 2 : 4 : 6-

tribromobenzoate and methyl 2 : 6-dibromobenzoate, is hydrolysed to the free acid when boiled with hydrazine hydrate, was prepared by boiling the acid chloride with a methyl-alcoholic solution of sodium methoxide. The following hydrazones were obtained by condensing acetaldehyde, benzaldehyde, acetone, or acetophenone with the appropriate hydrazide: *acetaldehyde-*2 : 4 : 6-*tribromobenzoylhydrazone*, needles, m. p. 221°; *benzaldehyde-*2 : 4 : 6-*tribromobenzoylhydrazone*, needles, m. p. 224°; *acetone-*2 : 4 : 6-*tribromobenzoylhydrazone*, needles, m. p. 221°; *acetophenone-*2 : 4 : 6-*tribromobenzoylhydrazone*, needles, m. p. 189°; *acetaldehyde-*2 : 6-*dibromobenzoylhydrazone*, plates, m. p. 190°; *benzaldehyde-*2 : 6-*dibromobenzoylhydrazone*, granules, m. p. 201°; *acetone-*2 : 6-*dibromobenzoylhydrazone*, granules, m. p. 230°; *acetophenone-*2 : 6-*dibromobenzoylhydrazone*, granules, m. p. 192°; *acetone-*3 : 5-*dibromo-*p-*toluoylhydrazone*, plates, m. p. 239°; *acetophenone-*3 : 5-*dibromo-*p-*toluoylhydrazone*, plates, m. p. 192°. C. K. I.

Dinitrotolylhydrazines. OSCAR LISLE BRADY and JOHN HERBERT BOWMAN (Trans., 1921, **119**, 894—900).

The Basic Amino-acids of Glycinin, the Globulin of the Soy Bean, *Soja hispida*, as determined by van Slyke's Method. D. BREESE JONES and HENRY C. WATERMAN (*J. Biol. Chem.*, 1921, **46**, 459—462).—Glycinin contains: arginine, 8·07%; cystine, 1·18%; histidine, 1·44%; lysine, 9·06%; ammonia, 2·28%; tryptophan, 1·37%. The figure for tryptophan is regarded as a minimal one. E. S.

Use of Chloroform for the Preparation of Active Nucleoproteins and Nucleic Acids in vitro in Blood. Complexity of the Action of Nucleic Acids in vitro. MAURICE DOYON (*Compt. rend.*, 1921, **172**, 1212—1214).—To obtain a very active thymonucleic acid, the thymus of a calf is allowed to autolyse in the presence of chloroform, before applying Neumann's method. The injection of nucleic acids into the vein of a dog provokes the secretion, probably by the liver, of an anti-coagulating nucleoprotein. They also cause narcosis, an extensive vasodilatation and lowering of the arterial pressure. W. G.

Nuclein Metabolism. XII. The Hydrolysis of Thymus-nucleic Acid by means of Picric Acid. The Composition of Thymic Acid. S. J. THANNHAUSER and BERTA OTTENSTEIN (*Zeitsch. physiol. Chem.*, 1921, **114**, 39—50. Compare A., 1919, i, 228).—As a result of the hydrolysis of thymus-nucleic acid with boiling aqueous picric acid, the authors isolated, as brucine salts, cytosine-hexose-mono- and -di-phosphoric acids, thymine-hexose-mono- and -di-phosphoric acids, and two other phosphoric acid complexes of undetermined constitution.

The di-phosphoric acids above-mentioned had already been obtained by Levene and Jacobs (A., 1912, i, 926), who regarded them as probably linked, in thymus-nucleic acid, by means of an oxygen bridge.

From the result of their picric acid hydrolysis, the authors conclude

that it is more probable that the thymus-nucleic acid molecule contains a complex consisting of the two mono-phosphoric acids linked together by a phosphoric acid bridge. Thymic acid (Kossel and Neumann, A., 1896, i, 658; Steudel and Brigl, A., 1911, i, 342) is not a pure substance. C. R. H.

Chemistry of Enzymes. TH. BOKORNY (*Allgem. Brau. Hopfenzeit.*, 1921, 121—122, 129—130, 133—134; from *Chem. Zentr.*, 1921, i, 911. Compare this vol., i, 369).—The action of nitrous acid on enzymes, whereby the nitrogen corresponding with the amide nitrogen present, is set free, has been studied. It was found necessary to work under standard conditions as to apparatus and amounts of reagents used. Pepsin was found to contain 3·16% of amide nitrogen; emulsin, 4·17%; rennet powder, 3·05%; hen-egg-albumin (Kahlbaum), 3·281%.

Trypsin in neutral solution is completely absorbed by kaolin and alumina; it is amphoteric, combining with 3% of ammonia and 2—5% of sulphuric acid. Pepsin in neutral solution is incompletely absorbed by kaolin, but completely by alumina; it is also amphoteric, but somewhat more acidic than basic; combination with acids and bases could not be demonstrated. Invertase in neutral solution is not absorbed by kaolin and only incompletely by alumina; it is acidic in character. G. W. R.

Course of the Reaction of Arginase. R. EBERHARD GROSS (*Zeitsch. physiol. Chem.*, 1921, **112**, 236—251).—At P_H 6·62 and 37°, the "constant," calculated for a unimolecular reaction, gradually decreases. The reaction stops at 70—85% conversion. Addition of urea does not inhibit the reaction, but ornithine does so markedly. This is probably due to an inactivation of the enzyme, rather than to the attainment of a chemical equilibrium (compare Edlbacher, A., 1916, i, 524; 1917, i, 670). G. B.

Preparation of Highly Active Saccharase (Invertase) Preparations. V. Phosphorus Content of Purified Saccharase Solutions after Exhaustive Dialysis, and the Micro-estimation of Phosphorus. HANS VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1921, **112**, 282—294. Compare A., 1920, i, 689; this vol., i, 202).—After complete dialysis of solutions, formerly described, the organic "high molecular" combined phosphorus is proportional to the activity of the enzyme. It was approximately estimated by Neumann's method (A., 1903, ii, 243; 1904, ii, 68) after micro-titration of the molybdate precipitate. G. B.

Poisoning of Amylase by Heavy Metals and Organic Substances. URBAN OLSSON (*Zeitsch. physiol. Chem.*, 1921, **114**, 51—71).—Experiments are described which show that silver nitrate, chloride, or cyanide, copper sulphate, free iodine, aniline, and phenylhydrazine, all have a toxic effect on amylase; of these substances the silver salts are the most toxic and aniline the least. With constant amounts of enzyme, the effect is proportional to the amount of poison; with constant amounts of poison, the effect increases with diminishing amounts of enzyme.

The toxic effect of silver is instantaneous; that of copper takes time to exert itself; in both cases the poisoning process appears to be accompanied by slight spontaneous regeneration. C. R. H.

Method of Action and Electrolytic Nature of Diastatic Ferments. A. HAHN (*Sitzungsber. Ges. Morph. Physiol. München*, 1919, **31**, 66; from *Physiol. Abstr.*, 1921, **6**, 113).—In diluted buffer solutions more acid than the optimum reaction for the particular ferment, neutral salts accelerated its activity; but in concentrated buffer solutions the neutral salt had a retarding effect. On the alkaline side of the optimum point, similar effects were observed, but although the accelerating effect of the neutral salt was much more marked in dilute buffer solutions, it never became reversed in the presence of high concentration of the buffers. The *iso*electric point of the ferments can be changed by the action of neutral salts without an appreciable change in the diastatic power or in the value of the reaction optimum. The electrolytic nature of these enzymes, therefore, has little influence on their activities. E. S.

Hydrolysis of α-Methyl-*d*-mannoside by Soluble Ferments. H. HÉRISSEY (*J. Pharm. Chim.*, 1921, [vii], **23**, 409—417. Compare this vol., i, 306).—The hydrolysis of α-methyl-*d*-mannoside proceeds slowly with emulsin decomposition amounting to 18% being observed after fifteen days at 32°. Emulsin therefore contains a small quantity of a specific ferment hydrolysing *d*-mannoside, to which the name α-d-*mannosidase* is given. A slight although well-marked hydrolysis was also observed with an aqueous extract of the ferments of *Aspergillus niger*, and hydrolysis to the extent of 46% was obtained after seventy-eight days at 32° by using the dried and powdered culture of *Aspergillus* itself. A maceration of brewer's yeast which rapidly decomposed methyl-*d*-glucoside had no action on the *d*-mannoside, although by using the entire yeast 25·8% hydrolysis was effected in thirty-three days at 28—30°. The most advantageous source of α-*d*-mannosidase found was the germinating seeds of lucerne. After forty days at 15—18°, the filtered aqueous extract of the dried and powdered germinating seed effected hydrolysis of the mannoside to the extent of 32·83%, whilst the dried powder itself added to the mannoside solution caused complete hydrolysis at 32° after about fifty days. G. F. M.

Organic Derivatives of Silicon. XXV. Saturated and Unsaturated Silicohydrocarbons, Si_4Ph_8. FREDERIC STANLEY KIPPING and JAMES EDWIN SANDS (Trans., 1921, **119**, 830—847).

Organic Derivatives of Silicon. XXVI. Piperidine as an Analytical Reagent. FREDERIC STANLEY KIPPING and JAMES EDWIN SANDS (Trans., 1921, **119**, 848—850).

Preparation of 5 : 5′-Mercuri-bis-3-nitro-4-hydroxyphenylarsinic Acid. JULIUS STIEGLITZ, MORRIS KHARASCH, and MARTIN HANKE (*J. Amer. Chem. Soc.*, 1921, **43**, 1185—1193).—The con-

stitution of 3-nitro-4-hydroxy-5-acetoxymercuriphenylarsinic acid obtained by Raiziss, Kolmer, and Gavron (A., 1920, i, 196) is confirmed by converting it into 4 : 6-di-iodo-*o*-nitrophenol, *5-iodo-3-nitro-4-hydroxyphenylarsinic acid* being obtained as an intermediate product. When a suspension of the above mercury compound in water is boiled with a solution of sodium thiosulphate, it yields 6 : 6′-mercuri-bis-2-nitrophenol; but if the sodium thiosulphate is replaced by sodium sulphide, the final product is 5 : *5′-mercuri-bis-3-nitro-4-hydroxyphenylarsinic acid*, which gives a crystalline ammonium salt. Mercury compounds of the type R·Hg·R may be differentiated from those of the type R·HgX, where R is an aryl radical and X is inorganic, by the fact that alkaline sodium stannite does not react with the former, whereas with the latter a precipitate of metallic mercury is obtained. W. G.

Organo-derivatives of Bismuth. IV. The Interaction of the Halogen Derivatives of Tertiary Aromatic Bismuthines with Organo-derivatives of Magnesium and Mercury. FREDERICK CHALLENGER and CHARLES FREDERICK ALLPRESS (Trans., 1921, **119**, 913—926).

Physiological Chemistry.

Anaerobic Respiration in some Pelecypod Molluscs: Its Relation to Glycogen. C. Berkeley (*J. Biol. Chem.*, 1921, **46**, 579—598).—The author has confirmed the observation of Collip (*J. Biol. Chem.*, 1920, **45**, 23) that *Mya arenaria*, like some bacteria, can produce carbon dioxide under anaerobic conditions, and has extended this observation to other species. Since in bacteria the phenomenon is closely connected with carbohydrates, the author attempted to correlate it with the glycogen content of the molluscs, but either no glycogen disappears, or (in one species) the consumption is too small to account for the carbon dioxide produced, on the assumption (of Mathews) that the oxygen used in respiration is derived from the splitting of water, of which the hydrogen would be used in reducing dextrose, derived from glycogen, to sorbitol, for instance. In sealed vessels, the animals remain alive for some days and do not give off any trace of gas, other than carbon dioxide, which is fixed as bicarbonate in the sea-water. G. B.

Blood Bicarbonate Levels following Administration of Sodium Hydrogen Carbonate. Stanley P. Reimann and Hobart A. Reimann (*J. Biol. Chem.*, 1921, **46**, 493—498).—Palmer and van Slyke's formula (A., 1918, i, 142) for the estimation of the rise of blood bicarbonate after oral administration of sodium hydrogen carbonate "is surprisingly accurate in normal individuals, but less so in various diseases." The form of the

curve showing the rise and fall after intravenous administration has been investigated in dogs, under various anæsthetics. E. S.

Comparison of Blood and Lymph Bicarbonate after Intravenous Injection of Sodium Hydrogen Carbonate. STANLEY P. REIMANN and M. D. SAUTER (*J. Biol. Chem.*, **46**, 499—502. Compare preceding abstract).—Curves showing the hydrogen carbonate content of blood and of lymph during and after intravenous injection of sodium hydrogen carbonate indicate that there is a rapid transference of hydrogen carbonate from the blood to the lymph. E. S.

The Potassium Content of Human Blood. V. C. MYERS and J. J. SHORT (*Proc. Soc. Exp. Biol. and Med.*, 1920, **18**, 72—73; from *Physiol. Abstr.*, 1921, **6**, 130).—Normal human serum contains somewhat less than 20 mg. of potassium per 100 c.c.; whole blood contains about eight to ten times this amount. In cases of nitrogen retention, the potassium content both of the serum and of the whole blood is increased. In general, the potassium content of whole blood tends to vary directly with the red cell content and the percentage of total solids. E. S.

Coagulation of the Blood. I. The Rôle of Calcium. H. W. C. VINES (*J. Physiol.*, 1921, **55**, 86—99).—The author describes a method for the estimation of calcium in 0·5—1 c.c. of blood (and other fluids) depending on coagulation. First, blood is mixed with ammonium oxalate solutions of different strengths, and the minimum amount of oxalate is found which will prevent coagulation for a given time. Secondly, to a series of tubes containing blood with this minimum quantity of oxalate, calcium solutions of known strength are added and the amount found which will induce complete clotting in a given time. Thirdly, the unknown blood, serum, or other solution at various dilutions is added instead of the calcium solutions of known content. Where free thrombin may be present, the blood or serum is first heated at 55° for an hour. The error ranges from about 0·15—0·25 mg. % in concentrations of calcium between 5 and 9 mg. %. [A somewhat similar method has been employed by N. Voorhoeve (A., 1911, ii, 126), but is not mentioned by the author.] Using his method, the author concludes that calcium is present in normal blood in two forms, ionised and combined as complex; the latter is transformed into the ionic state during coagulation. Oxalate, citrate, or fluoride added in amounts equivalent to the total calcium does not inhibit coagulation; this indicates that the presence of ionised calcium is not essential to the clotting process. Anti-coagulants all inhibit clotting by combining with the calcium-containing complex, in amounts in excess of the chemical equivalent of the calcium. Calcium combined with an unknown organic substance is the essential factor in blood coagulation; this complex probably corresponds with the thrombokinase of Morawitz (A., 1904, ii, 59, 353). (Compare also Rona and Takahashi, A., 1911, ii, 302.) G. B.

Nuclein Metabolism. XI. The Action of Human Liver-extract on Nucleotides (Guanosine, Adenosine, Xanthosine). S. J. THANNHAUSER and BERTA OTTENSTEIN (*Zeitsch. physiol. Chem.*, 1921, **114**, 17—27).—Solutions of guanosine and adenosine were subjected to the action of aqueous extracts of fresh human liver, with free access of air. Even after short periods the authors were able to isolate free xanthine and uric acids; in no case was there found guanine, adenine, or xanthosine, although in certain cases some of the original nucleotides were still present. Xanthosine under similar conditions gave xanthine and uric acid, but no trace of a uric acid nucleotide.

The authors conclude that, probably, in normal metabolism, de-amination and decomposition of the purine-carbohydrate complex occur simultaneously; and that consequently adenine and guanine are not normal intermediate products of nuclein metabolism.

C. R. H.

The Relation of Plant Carotinoids to Growth and Reproduction of Albino Rats. LEROY S. PALMER and CORNELIA KENNEDY (*J. Biol. Chem.*, 1921, **46**, 559—577).—A review of the literature on the relationship between carotinoids and vitamin-*A* is given and the non-identity of the latter with carotin confirmed. Carotinoids do not occur in the albino rat. E. S.

Amino-acids in Nutrition. III. Is Proline a Growth-Limiting Factor in the Proteins of Peas (*Vicia sativa*)? What Nucleus in Zein is responsible for Supplementing these Proteins? BARNETT SURE (*J. Biol. Chem.*, 1921, **46**, 443—452).—The conclusion of McCollum, Simmonds, and Parsons (A., 1919, i, 186) that zein supplements the proteins of peas is confirmed. Experiments on rats are described showing that neither addition of the proteins arachin and edestin, nor of the amino-acids alanine, valine, tryptophan, lysine, cystine, tyrosine, and proline, to the diet improves the nutritive value of the pea proteins. It is therefore suggested that zein may contain an amino-acid necessary for growth which has not yet been isolated. E. S.

Utilisation of Xylose by Animals. ELBERT W. ROCKWOOD and KRIKOR G. KHOROZIAN (*J. Biol. Chem.*, 1921, **46**, 553—558).—From experiments on rabbits, cats, dogs, and man in which the difference in the amount of xylose ingested by the mouth and that passed in the urine and fæces is measured, it is concluded that there is a low limit to the amount of xylose which can be utilised by animals. Less xylose is used when the diet is rich, than when it is poor in other carbohydrates. E. S.

Mechanism of Action of Becquerel Rays on the Function of Cells. W. ENGELMANN (*Strahlentherapie*, 1920, **11**, 287—291; from *Physiol. Abstr.*, 1921, **6**, 117).—The perfusion of blood containing radium emanation through the surviving liver does not lead to an increase in the production of acetoacetic acid. An

increase is observed, however, if the animal has been given water containing the emanation during the day before the experiment.

E. S.

The Effect of Age on Pancreatic Enzymes. FREDERIC FENGER and MARY HULL (*J. Biol. Chem.*, 1921, **46**, 431—435. Compare A., 1919, i, 461).—Pancreas preparations stored for one year show considerable loss in diastatic and lipolytic activities; the proteolytic activities, however, remain constant, indicating that trypsin is the most stable of the pancreatic enzymes. E. S.

Regulation of the Supply of Energy in Muscular Contraction. W. HARTREE and A. V. HILL (*J. Physiol.*, 1921, **55**, 133—158).—The heat given out by stimulated frog's muscle has been measured at various temperatures, and from the temperature coefficients conclusions are drawn as to the chemical mechanism. With a prolonged maximal stimulus there is a sudden outburst of heat during the first moment; succeeding elements of the stimulus produce less and less effect, until a steady state (dynamic equilibrium) is reached, in which heat is produced at a constant rate. In this stage the rate of heat production has a temperature coefficient of 2·8 for a rise of 10°, and is similar to that of an ordinary chemical reaction. The muscles are not allowed to contract, and if the tension set up in them is considered, it is found that for prolonged contractions the heat-production finally becomes proportional to the tension maintained. The rate of heat-production per unit of force maintained (tension) is increased 2—3 times by a rise of 10°. Therefore the "efficiency" of a muscle is much greater at low than at high temperatures.

These and other facts suggest as mechanical analogy a large reservoir of compressed air, connected by a narrow tube to an elastic bag with a release valve. When the valve is momentarily opened, the air rushes out, at first rapidly, and then more slowly until the rate of outflow reaches a value determined by the bore of the connecting tube. Chemically, the large reservoir of energy is the store of glycogen in the muscle, the narrow tube is a catalyst, transforming the glycogen into lactic acid. The elastic bag is a balanced action, carbohydrate $\rightleftharpoons$ lactic acid. The opening of the valve is probably represented by a temporary permeability to lactic acid, produced by the stimulus in some membrane. The lactic acid escapes and causes a change in colloidal properties, resulting in contraction of the muscle fibres. In the later stages of prolonged stimulation the lactic acid is removed at the same rate at which it is supplied. Its concentration in the sensitive structure would be proportional to the rate of supply, and as the former would be measured by the tension of the muscle and the latter by the heat given out, the tension and heat given out would be in a proportion constant for each temperature. This is indeed the case, as was pointed out above. The high temperature coefficient of the ratio (2—3 times for 10°) indicates that the mechanism of removal of the lactic acid is a chemical and not a physical process. In a previous paper, the authors have shown the rate

of relaxation to have a temperature coefficient of 2·2. Since the energy liberated by the change from dextrose to lactic acid is only about 16% of the heat given out, the discovery for the acid of a precursor other than dextrose has often been attempted, but in vain. The present theory obviates the need of such a precursor. Most of the heat given out is obtained, not from chemical energy, but from potential energy provided by the effect of lactic acid on some "active" structure or surface. "We are reduced rather to finding a non-oxidative chemical or physico-chemical reaction, capable of seizing on and removing lactic acid from the sensitive structures or surfaces of the muscle, and then of delivering up the lactic acid it has seized on to the later and gradual processes of oxidative recovery." G. B.

Chemistry of Lactacidogen. III. GUSTAV EMBDEN and FRITZ LAQUER (*Zeitsch. physiol. Chem.*, 1921, **113**, 1—9).—In support of the view expressed previously (A., 1915, i, 344, 345) that the lactic acid in muscle originates from a hexose-phosphoric acid complex, the authors reported the isolation (A., 1917, i, 674) of an osazone which was identical with that previously obtained by Lebedev (A., 1909, i, 863) and by Young (A., 1911, i, 422) from yeast-hexose-diphosphoric acid. They now give complete details of the elaborate precautions necessary for the isolation of the osazone; the yield of pure substance from dog's muscle was 0·05%.

The authors do not claim to have established the identity of "lactacidogen" (the substance in striped muscle which gives rise to lactic acid, A., 1912, ii, 1072) with the yeast-hexose-diphosphoric acid, but they regard the osazone which they have obtained as certainly a derivative of lactacidogen. C. R. H.

Influence of Muscular Work on the Lactacidogen Content of Striped Muscle. GUSTAV EMBDEN, ERNST SCHMITZ, and PETER MEINCKE (*Zeitsch. physiol. Chem.*, 1921, **113**, 10—66).—Owing to the rapidity of the breakdown of lactacidogen in finely divided muscle at body temperature, estimations of inorganic phosphorus in freshly-removed muscle, and in the same muscle after remaining for one and two hours at 40° in a finely divided condition, give indications of the amount of lactacidogen originally present.

(1) Diet and moderate doses of phloridzin have no effect on the content of lactacidogen.

(2) In rabbits, severe muscular work of short duration, following the administration of phloridzin, and in rabbits and dogs strychnine convulsions, cause a marked diminution in the lactacidogen content of the muscle.

(3) The increase of lactic acid in these experiments on the whole animal is, proportionately, not so great as that of phosphoric acid; whereas, on tetanising an isolated frog's muscle, an increase in the lactic acid is observed without a concomitant increase in the phosphoric acid. This is explained by the effect of the different experimental conditions on the relative velocity of the breakdown of lactacidogen and its re-synthesis from phosphoric acid and fresh

carbohydrates. Former estimations of inorganic phosphorus in muscle must have given results which were too high owing to the rapidity of the breakdown of lactacidogen. C. R. H.

Raising of the Capacity for Work by Administration of Phosphate. GUSTAV EMBDEN, EDUARD GRAFE, and ERNST SCHMITZ (*Zeitsch. physiol. Chem.*, 1921, **113**, 67—107).—Numerous experiments on soldiers (with an ergostat and by marching) and on miners show that 7·5 grams of sodium dihydrogen phosphate per day increase the capacity for muscular work, presumably by facilitating the re-synthesis of lactacidogen. A favourable effect on the nervous system is also claimed. Some observations were also made on horses. C. R. H.

Influence of Muscular Work upon Excretion of Phosphoric Acid. GUSTAV EMBDEN and EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1921, **113**, 108—137).—A few hours' hard work with an ergostat considerably increased the urinary phosphate in two trained individuals. The contradictory results of some earlier observers are attributed to their not having been in training. It seems that in hard work the muscles take up from the blood, not only more sugar, but also more phosphoric acid. C. R. H.

Lactacidogen Content of Frog's Muscle. AMELY CAMILLA WECHSELMANN (*Zeitsch. physiol. Chem.*, 1921, **113**, 146—173). **Influence of External Temperature on the Lactacidogen Content of Frog's Muscle. I and II.** E. ADLER (*ibid.*, 174—186), E. ADLER and L. GÜNZBURG (*ibid.*, 187—192). **Influence of the Season of the Year on the Lactacidogen Content of Frog's Muscle.** E. ADLER (*ibid.*, 193—200). **Distribution of Phosphoric Acid in the White and Red Musculature of the Rabbit.** GUSTAV EMBDEN and ERICH ADLER (*ibid.*, 201—222). **Lactacidogen–Phosphoric Acid and the Residual Phosphoric Acid Content in the Muscles of Fowls and Pigeons.** GEORG LYDING (*ibid.*, 223—244). **Distribution of Phosphoric Acid in the Thigh Muscles of the Toad.** PANOS PANAJOTAKOS (*ibid.*, 245—252). **Influence of Muscular Work on the Lactacidogen Content of the Red and White Musculature of the Rabbit.** FELIX COHN (*ibid.*, 253—262). **Influence of Phosphorus Poisoning on the Lactacidogen Content of Rabbit's Muscle.** GUSTAV EMBDEN and S. ISAAC (*ibid.*, 263—270). **Influence of Phosphorus Poisoning on the Lactacidogen Content of Frog's Muscle.** E. ADLER and S. ISAAC (*ibid.*, 271—280). **Influence of Fever on the Phosphoric Acid Content of [Rabbit's] Muscle.** A. ADAM (*ibid.*, 281—300). **Mechanism by which External Temperature Influences the Lactacidogen Content of Frog's Muscle.** HEINZ LAWACZECK (*ibid.*, 301—312).—These twelve papers all support the contention that where muscular activity is greatest there is most lactacidogen. In cold-blooded animals (frog), there is more at 30° than at 0° and the mechanism of the change is not a nervous one, as it occurs in muscles with cut nerve supply. When, with rise of temperature, the lactacidogen increases the

residual phosphorus diminishes. On cooling summer frogs, the reverse changes occur. The seasonal changes are correlated with muscular activity. The white muscles of rabbits contain about twice as much lactacidogen as the more sluggish red muscles, which latter, on the other hand, are richer in non-lactacidogen phosphorus, regarded as a reserve. The breast muscles of the pigeon have a greater reserve of residual phosphorus than those of the fowl. The toad has greater content than the frog, for, although slower, the former does more work. Muscular work and strychnine convulsions decrease lactacidogen in the white muscles of the rabbit, but not in the red, where, owing to slower action, there is given time for its re-synthesis. Phosphorus poisoning (which is accompanied by great muscular weakness) and Nagana fever have a similar effect. C. R. H.

Choline as a Precursor of Creatine. W. F. SHANKS (*Proc. Physiol. Soc.*, 1921, viii—ix, *J. Physiol.*, **55**).—Repetition, by a slightly different method, of the experiments of Riesser (A., 1913, i, 1135). Choline injected intravenously into a rabbit increased the creatine content of muscle in three hours from an average of 1·90% to one of 1·99%. The experiments are not incompatible with Riesser's theory of the conversion of choline into creatine by linking with urea, partial demethylation, and oxidation. G. B.

Creatine and Muscle Tonus in Man. F. S. HAMMETT (*J. Amer. Med. Assoc.*, 1921, **76**, 502—503; from *Physiol. Abstr.*, 1921, **6**, 120).—Estimations on the blood of a man in a state of catatonic stupor for eight weeks showed increase of creatine during re-establishment of normal muscular tone. The observations support the view that creatine is a normal end-product of protein katabolism. E. S.

Substances Needed for the Growth of a Pure Culture of *Colpidium colpoda*. R. A. PETERS (*J. Physiol.*, 1921, **55**, 1—32). —The author describes a method for the culture and subculture during a year of this ciliate protozoon, starting from a single individual. The cultures are regarded as free from bacteria and other organisms. Contrary to the view that even the lowest forms of animal life are not satisfied with a source of carbon less complex than dextrose, *Colpidium* will live on ammonium glycerophosphate and inorganic salts, but compounds with only two carbon atoms are inadequate. Ammonium, phosphate, chloride, potassium, and magnesium are all essential in silica tubes, but glass tubes supply enough of the last two elements. Uranium cannot replace potassium, so that the effect of the latter is not merely a radioactive one as implied by Zwaardemaker (*Ann. Reports*, 1919, **16**, 148; A., 1920, i, 343, 345, 511; ii, 279). Loeb (this vol., i, 145) has reached a similar conclusion. G. B.

Bioluminescence. IV. The Nature of the Luciferase of *Cypridina Helgendorfii*. S. KANDA (*Amer. J. Physiol.*, 1921, **55**, 1—12; from *Physiol. Abstr.*, 1921, **6**, 114).—After precipitation by mercuric chloride of extracts of this organism containing

luciferase, the clear filtrate gives most of the protein reactions. The luciferase is contained in the precipitate produced by phosphotungstic acid, by potassium ferrocyanide and acetic acid, by saturation with magnesium sulphate, by half-saturation with ammonium sulphate, or by acetone and alcohol. It is coagulated at about 65°. It passes slowly through parchment paper. The results do not decide the question whether it is a protein or merely adsorbed on the precipitates produced. E. S.

The Chlorine Content of Milk and Blood after the Ingestion of Sodium Chloride. W. DENIS and WARREN R. SISSON (*J. Biol. Chem.*, 1921, **46**, 483—492).—The administration of sufficiently large doses of sodium chloride to lactating goats produces an increase in the chlorine content both of the milk and of the blood plasma. Simultaneously with this increase, there is a great diminution in the volume of milk. E. S.

The Rate of Nitrogen Elimination. W. S. MCELLROY and H. O. POLLOCK (*J. Biol. Chem.*, 1921, **46**, 475—481).—Measurements were made of the nitrogen elimination and of the urea and non-protein nitrogen of the blood of dogs fed on lean meat. It is concluded from the results that the rate of nitrogen elimination is an index of the rate of digestion and absorption. E. S.

The Nature of Ehrlich's Diazo reaction. I and II. LEO HERMANNS and P. SACHS (*Zeitsch. physiol. Chem.*, 1921, **114**, 79—87, 88—93).—Two methods are described for the separation from urine of the substances which give the diazo-reaction. The first method consists in combining these substances with di-chloro-diazobenzene chloride and extracting the azo-dyes formed with a mixture of ether and pyridine; the second in the direct extraction of the substance with ether from the highly concentrated, acidified urine. By the first method the authors obtained an azo-dye containing sulphur; by the second, a solution containing a reducing substance which gave an intense diazo-reaction and also gave Ehrlich's aldehyde reaction on warming.

The isolation is described, from the urine of a patient with carcinoma of the liver, by the first method, of an azo-dye of the formula $C_{16}H_{11}O_3N_3Cl_2$. The coupling substance, $C_{10}H_9O_3N$, which was present in the urine, the authors consider, in view of its specific reactions, to be 4-hydroxyindole-3-acetic acid. They regard this substance as a degradation product of tryptophan. C. R. H.

Proteolytic Enzymes in Normal and Pathological Urines. S. G. HEDIN (*Zeitsch. physiol. Chem.*, 1921, **112**, 252—281).—Dialysed urines were made to act on casein and on Witte peptone at P_H 8 and on casein at P_H 1·6. Peptone is the most sensitive substrate and gives clear indications with normal urines, and more obviously with the urine from the fever stage of pneumonia. G. B.

Physiological Action of Acids and their Solubility in Lipoids. M. PHILIPPSON and G. HANNEVART (*Compt. rend. soc. biol.*, 1920, **83**, 1570—1572; from *Physiol. Abstr.*, 1921, **6**, 119).—Organic acids at $0·01N$-concentration have an inhibitory action on

muscular contraction, the power of each acid depending on its position in the ascending series—formic, glyceric, lactic, tartaric, acetic, propionic, malic, and butyric. The diffusibility of these acids through a collodion membrane charged with a lipoid follows a similar order. Inorganic acids behave oppositely on muscle, whilst the artificial lipoid membrane is impermeable to them.

E. S.

Chemistry of Vegetable Physiology and Agriculture.

The Effect of Organic Nitrogenous Compounds on the Nitrate-forming Organism. E. B. FRED and AUDREY DAVENPORT (*Soil Sci.*, 1921, **11**, 389—407).—The experimental data do not furnish any evidence in support of the statements of Beijerinck that the nitrate-forming organism when grown in the presence of certain organic substances loses its power of oxidation. It was found that certain forms of organic matter benefit rather than injure these organisms. W. G.

Influence of Electric Potential on the Velocity of Fermentation. M. C. POTTER (*Proc. Univ. Durham Phil. Soc.*, 1915—1920, **6**, 16—21).—It was shown previously (A., 1911, ii, 913) that a rise of potential amounting to 0·3—0·5 volt is produced by yeast when growing in an ordinary fermentable liquid. The experiments now described show that the fermentation of dextrose solution by commercial yeast proceeds exactly similarly in an "earthed" flask as in one maintained at a potential of +210 volts. T. H. P.

Carbon Nutrition in Cultivated Plants. BORNEMANN (*Ang. Bot.*, 1920, **2**, 284—290; from *Chem. Zentr.*, 1921, i, 840—841).—All the necessary carbon for plants is provided by soil carbon dioxide and when all other growth factors are at optimum, increased growth can only be obtained by an increase in the amount of carbon dioxide originating from the soil. With decrease of carbon dioxide in the air surrounding the plants, the small amounts of carbohydrate formed are required for the elaboration of the nitrogen obtained by the roots and a purely vegetative type of growth results. Young plants, when the partial pressure of carbon dioxide is increased, show at first an increase in vegetative growth; the older cells, however, soon become lignified, and premature development of flowering processes, where possible, occurs. If the plant has storage organs, storage begins prematurely with inhibition of vegetative growth. With the carbon dioxide partial pressure at a maximum, vegetative growth is suspended and all assimilated material stored directly. With further increase of the carbon dioxide content asphyxia occurs. G. W. R.

Organic Chemistry.

Molecular Rearrangement of Unsaturated Compounds in Acid Solution. ALF. GILLET (*Bull. Soc. chim. Belg.*, 1921, **30**, (6), 138—153. Compare Gillet, this vol., i, 490).—A theoretical discussion of some types of intramolecular rearrangement which follow on dehydration. In certain of the examples quoted the rearrangement depends on the production of a bivalent carbon atom and its subsequent transformation with production of an ethylenic linking by the shifting of a group, whilst in others, for example, tertiary alcohols, it is impossible to interpret the mechanism of rearrangement in such a manner. The former case is referred to as the methylene, the latter as the ethylene transformation.

The conclusions drawn, which are derived from the consideration of a variety of reactions, are embodied in the following rules:

When a mono-substituted bivalent carbon atom results from dehydration, the most positive group attached to the next carbon atom moves from the latter to the former. The addition of alkyl groups to unsaturated carbon atoms takes place in such a way as to produce the most symmetrical molecule possible by leaving the two carbon atoms taking part in the change with the greatest possible similarity in their attached groups. The converse holds for the subtraction of alkyl groups. In cases of ring formation where the carbon atoms concerned are not adjoining, the rule also obtains.

Ethylenic transformation takes place most readily when the hydrogen atom which is split off together with the OH-group is linked to the carbon atom bearing the less positive groups (compare Saytzew, *Annalen*, 1875, **179**, 296), and also if the hydroxyl group is attached to the more positively saturated carbon atom (compare Markownikov, *Annalen*, 1869, **153**, 256). In the case of hydration of an ethylenic group, the rule also applies. When a ring is opened by taking up water, the break occurs between the two carbon atoms, which are linked to the most unlike substituents, and the hydrogen atom combines with the more negatively, the OH-group with the more positively saturated of the two carbon atoms. The converse case, in which a ring is formed by dehydration, follows a similar rule. It is pointed out that this is only a special case, as ethylene itself may be regarded as a ring of two carbon atoms.

The suggestion is made that organic groups should be arranged in an electro-positive series. H. J. E.

Brodie's Hydrocarbon, Melene, $C_{30}H_{60}$. YNGVE FUNCKE (*Arch. Pharm.*, 1921, **259**, 93—101).—Re-examination of the products of the dry distillation of bees-wax has led the author to the conclusion that Brodie's hydrocarbon, melene, has not yet been isolated in the homogeneous condition.

The wax was mixed with an equal amount of infusorial earth and twice distilled with a free flame from an iron vessel. The distillate was treated with steam, and the volatile and non-volatile portions were subsequently separately subjected to fractional distillation. It is found that mixtures of saturated and unsaturated hydrocarbons, together with small amounts of oxygenated compounds, are produced. The unsaturated substances predominate in the fractions of lower boiling point, whilst saturated compounds are the chief components of the higher boiling fractions. The production of hydrocarbons of high molecular weight depends on the rate of distillation, and is favoured by rapidity in this process. The solid hydrocarbons which are obtained from the residue left after the distillation of the more volatile substances can be separated by cold ether into two groups, one of which comprises products containing about twenty-five carbon atoms, whilst in the other substances about thirty carbon atoms are present. The separation of these groups into their individual components could not be effected by physical methods. After conversion of the unsaturated hydrocarbons into their bromides, however, it was found possible to isolate hextriacontane, $C_{31}H_{64}$, m. p. 68°. H. W.

The Catalytic Decomposition of Polyhalogenated Aliphatic Hydrocarbons. ALPHONSE MAILHE (*Compt. rend.*, 1921, **172**, 1582—1584. Compare A., 1904, i, 277; 1905, i, 334).—ααββ-Tetrachloroethane, when passed with hydrogen over nickel at 300—320°, gives αβ-dichloroethylene and hydrogen chloride. Under similar conditions ααββ-tetrabromoethane gives αβ-dibromoethylene; β-chloro-αβ-dibromopropane gives β-chloropropylene; αβ-dichloro-αβ-dibromoethane gives αβ-dichloroethylene, and ααβ-trichloro-αβ-dibromoethane gives ααβ-trichloroethylene.

When ααββ-tetrabromoethane is passed over barium chloride at 400—420° it gives αβ-dibromoethylene and ααβ-tribromoethylene, and trichlorodibromoethane gives bromine and trichloroethylene. W. G.

Preparation of Triaryl and Trialkyl Derivatives of Iodine. VICTOR ARREGUINE and EDUARDO D. GARCÍA (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 121—128).—The authors attempted to prepare triaryl and trialkyl derivatives of iodine. By the Friedel and Crafts' reaction with iodine trichloride and benzene, chloro-substitution products of benzene were obtained, together with small quantities of iodobenzene: derivatives of tervalent iodine were not obtained. Grignard's reaction both with iodine trichloride and with iodobenzene dichloride gave equally unsuccessful results. In the case where iodobenzene dichloride was used, iodobenzene and diphenyl were formed. G. W. R.

Vapour Pressures of Mixtures of 95% Ethyl Alcohol and Ethyl Ether. L. J. OLMER (*Bull. Soc. chim.*, 1921, [iv], **29**, 382—385).—The author has plotted the vapour pressure curves of mixtures of 95% ethyl alcohol and ethyl ether, containing 0, 10, 20, 40, 60, 80, or 100% of ether over the temperature range —20°

to $+20°$. The results are fairly well represented by the equation $P=a+(b-a)x^n$, where P is the pressure of the mixture, a and b are the maximum pressures of the alcohol and ether at the temperature considered, x is the percentage of ether in the liquid, and n a constant equal 0·7. W. G.

Composition of the Gaseous Phase of Ethyl Alcohol–Ethyl Ether Mixtures in Terms of the Liquid Phase. L. J. OLMER (*Bull. Soc. chim.*, 1921, [iv], **29**, 385—389. Compare preceding abstract).—Curves are given showing the composition of the gaseous phase, as a function of the temperature, as a function of the liquid phase, and as a function of the pressure for mixtures of ethyl alcohol and ethyl ether containing 5, 10, 20, 50, or 75% of ether over the temperature range $-20°$ to $+30°$. W. G.

Action of Boric Acid on Glycerol and the Multivalent Alcohols. Application of a New Physico-chemical Volumetric Method. RENÉ DUBRISAY (*Compt. rend.*, 1921, **172**, 1658—1660).—Using the temperatures of miscibility with phenol as a guide to the formation of compounds (compare A., 1920, ii, 508, 756), the results obtained with boric acid and glycerol do not indicate the formation of any compound. With mannitol and boric acid, a compound is apparently formed, but is dissociated in the aqueous solution (compare Fox and Gauge, T., 1911, 1075). Similarly, with glycerol, boric acid, and sodium hydroxide a compound is probably formed, but is certainly dissociated. W. G.

α-Monosodium Glyceroxide: Its Structure and Application. ARTHUR FAIRBOURNE and HAROLD TOMS (T., 1921, **119**, 1035—1040).

Complex Compounds of Lead Acetate. R. WEINLAND (*Zeitsch. angew. Chem.*, 1921, **34**, 354).—A number of salts have been prepared from lead acetate by treatment with perchloric acid or its sodium salt. Examples of such salts, which may contain complex anions or kations or both, are: $\left[Pb^{ClO_4}_{(CH_3\cdot CO_2)_2}\right]Na$; $\left[Pb_2{}^{ClO_4}_{(CH_3\cdot CO_2)_4}\right]Na$; $\left[Pb_4{}^{(ClO_4)_5}_{(OH)_4}\right]Na$; $[Pb_2(CH_3\cdot CO_2)_3]ClO_4$; $[Pb_3(CH_3\cdot CO_2)_4](ClO_4)_2$; $[Pb_3(CH_3\cdot CO_2)_5]ClO_4$; and $[Pb(CH_3\cdot CO_2)_6][Pb(ClO_4)_4],3H_2O$. Basic lead perchlorates, soluble in water, are: $3Pb(ClO_4)(OH),2H_2O$; and $Pb_3(ClO_4)_2(OH)_4$. The compounds are generally insensitive to friction, but explode if heated above their melting point. W. J. W.

Preparation of Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 334554; from *Chem. Zentr.*, 1921, ii, 1019—1020).—Ethylidene diacetate is prepared by the action of acetylene on acetic acid in the presence of mercury salts of aromatic- or aliphatic-sulphonic acids. The mercury sulphonates exhibit strong catalytic activity, and acetylene combines rapidly with acetic acid at low temperatures (40—65°). The mercury salts of benzenesulphonic, naphthalenesulphonic, and camphorsulphonic

acids may be used but the mercury salts of aliphatic sulphonic acids are more satisfactory, for example, those of sulphoacetic acid, acetaldehydedisulphonic acid, and methanedisulphonic acid. Examples are given of the use of mercury naphthalene-β-sulphonate and mercury sulphoacetate. G. W. R.

Catalytic Decomposition of the Bromoacetic Acids and of Mixtures of Bromine and Acetic Acid. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1921, **172**, 1585—1587. Compare this vol., i, 157).—Using animal black as catalyst, it is shown that the bromoacetic acids are more readily decomposed by heat than the chloroacetic acids. Bromoacetic acid is decomposed according to the equations $CH_2Br{\cdot}CO_2H=CH_3Br+CO_2$ and $CH_2Br{\cdot}CO_2H=HBr+H_2O+CO+C$. With dibromoacetic acid, the changes are $CHBr_2{\cdot}CO_2H=CH_2Br_2+CO_2$ and $2CHBr_2{\cdot}CO_2H=CHBr_3+HBr+CO_2+CO+H_2O$. With tribromoacetic acid, the principal change is $CBr_3{\cdot}CO_2H=CHBr_3+CO_2$. With a mixture of bromine and acetic acid, the first effect is for the bromine to attack the acetic acid, giving tri- and di-bromoacetic acids and a little monobromoacetic acid, which then decompose, giving bromoform, dibromomethane, and methyl bromide, which may, however, be attacked by any residual bromine to give tetrabromomethane. In this way, 3 mols. of bromine react with 1 mol. of acetic acid. W. G.

The Higher Terms of the Saturated Fatty Series. ALBERT GASCARD (*Ann. Chim.*, 1921, [ix], **15**, 332—389).—A full account of work already published (A., 1920, i, 418, 470). W. G.

Acrylic Acid and Esters. Halogenated Propionic Acids and Esters. CHARLES MOUREU, MARCEL MURAT, and LOUIS TAMPIER (*Ann. Chim.*, 1921, [ix], **15**, 221—252).—A detailed study of the preparation of acrylic acid from acraldehyde by passage through β-chloropropionic acid is recorded. Acrylic acid, carefully purified, had m. p. 12·3°; b. p. 141·6°/752 mm.; d_4^{12} 1·0600; d_4^{20} 1·0511; n_D^{20} 1·4224. The acid is extremely sensitive to ultra-violet rays and to heat, probably undergoing polymerisation, being converted into a white solid. It readily reacts with the hydrogen haloids to give the corresponding β-halogenated propionic acids. Acrylic acid is readily esterified by heating the acid with the requisite alcohol in slight excess and 10% of sulphuric acid. The esters are readily converted into halogenated propionic esters and the β-halogenated propionic esters when heated with diethylaniline are reconverted into the acrylic esters. The following esters are described. Methyl acrylate, b. p. 80·7°/761 mm.; d^0 0·9735; d^{15} 0·9564; d^{18} 0·9558; n_D^{18} 1·4117; ethyl acrylate, b. p. 99·8°/761 mm.; d^0 0·9425; d^{15} 0·9245; d^{18} 0·9238; n_D^{18} 1·4072; *butyl acrylate*, b. p. 59°/25 mm.; 138—140°/756 mm.; d^0 0·9202; d^{12} 0·9117; d^{15} 0·9110; n_D^{12} 1·4254; iso*amyl acrylate*, b. p. 71—72°/72 mm.; 157—159°/753 mm.; d^0 0·9188; d^{12} 0·9070; d^{15} 0·9022; n_D^{12} 1·4287; allyl acrylate, b. p. 72°/27 mm.; d^0 1·0001; d^9 0·9945; d^{15} 0·9886; n_D^9 1·4390; *benzyl acrylate*, b. p. 110—111°/8 mm.; 228°/760 mm.

d^0 1·0789; d^8 1·0690; d^{15} 1·0630; n_D^8 1·5232; *menthyl acrylate*, b. p. 128°/18 mm.; d^0 0·9378; d^{15} 0·9310; n_D^{15} 1·4624.

Methyl β-chloropropionate, b. p. 148—150°/760 mm.; d^0 1·2036; d^{12} 1·1874; d^{15} 1·1861; n_D^{12} 1·4319; ethyl β-chloropropionate, b. p. 80°/29 mm.; 162·5°/761 mm.; d^0 1·1315; d^{15} 1·1141; n_D^{15} 1·4284; *butyl β-chloropropionate*, b. p. 97°/15 mm.; 104°/22 mm.; d^0 1·0814; d^9 1·0728; d^{15} 1·0708; n_D^9 1·4385; *iso*amyl β-chloropropionate, b. p. 121°/30 mm.; d^0 1·0544; d^{11} 1·0443; d^{15} 1·0419; n_D^{11} 1·4380; *benzyl β-chloropropionate*, b. p. 154—155°/13 mm.; d^0 1·1947; d^{12} 1·1813; d^{15} 1·1809; n_D^{12} 1·5234.

Methyl β-bromopropionate, b. p. 80°/27 mm.; d^0 1·5122; d^{15} 1·4897; d^{17} 1·4880; n_D^{17} 1·4603; ethyl β-bromopropionate, b. p. 112°/44 mm.; d^0 1·4409; d^{18} 1·4123; n_D^{18} 1·4569; *butyl β-bromopropionate*, b. p. 122·5°/18 mm.; 130°/26 mm.; d^0 1·3011; d^9 1·2773; d^{15} 1·2609; n_D^9 1·4577; iso*amyl β-bromopropionate*, b. p. 110—111°/11 mm.; d^0 1·2434; d^9 1·2323; d^{15} 1·2217. Ethyl β-iodopropionate, b. p. 116—117°/45 mm.; d^{15} 1·7040. Methyl αβ-dibromopropionate, b. p. 115°/25 mm.; d^0 1·9605; d^{17} 1·4499; n_D^{17} 1·5147; ethyl αβ-dibromopropionate, b. p. 112°/23 mm.; d^0 1·8188; d^{16} 1·7882; n_D^{16} 1·5015. (All the densities are relative to water at 4°.) W. G.

The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. I. Linseed Oil and its Fatty Acids. SAMUEL COFFEY (T., 1921, **119**, 1152—1161).

The γ-Chloroacetoacetic Esters. J. F. HAMEL (*Bull. Soc. chim.*, 1921, [iv], **29**, 390—402).—By a slight modification of Alexandrov's method (A., 1913, i, 443), using magnesium activated with mercuric chloride and working in ethereal solution, the author has prepared a number of γ-chloroacetoacetates from the corresponding chloroacetic esters.

Methyl γ-chloroacetoacetate has b. p. 96—97°/18 mm.; d^0 1·3048; n_D^{19} 1·4590; and gives a *copper* salt, m. p. 173—174°. Ethyl γ-chloroacetoacetate gives a *nickel* salt, m. p. 131—132°; a *zinc* salt, m. p. 121°, a *magnesium* salt, m. p. 170°, and *aluminium, manganese, lead, bismuth*, and *cobalt* salts, and with thiocarbamide gives ethyl aminothiazylacetate, m. p. 98·5°. iso*Butyl γ-chloroacetoacetate*, b. p. 118°/11 mm.; d^0 1·1426; n_D^{17} 1·45212, gives a *copper* salt, m. p. 131°. If, in the preparation of these esters, the activated magnesium is replaced by aluminium amalgam, such good yields are not obtained. W. G.

Inorganic Complex Salts. I. Potassium Ferrioxalate and Potassium Cobaltimalonate. WILLIAM THOMAS (T., 1921, **119**, 1140—1145).

Ferri-oxalic (Malonic) Acid Compounds. R. F. WEINLAND and FR. W. SIERP (*Zeitsch. anorg. Chem.*, 1921, **117**, 59—83).—Experiments made with the object of determining whether complex kations can be prepared containing oxalic acid and tervalent iron led to the discovery of new series of salts containing complex ferri-oxalic anions. Pyridine and other salts of chloro-oxalato-ferric

acids were obtained from solutions containing different proportions of their constituents. These salts are derived from the acids $[Fe(C_2O_4)Cl_2]H$, $[Fe(C_2O_4)_2H_2O,Cl]H_2$, and $[Fe(C_2O_4)_2Cl_2]H_3$. Only the salts of the first of these acids can be recrystallised from water. The pyridine and quinoline salts were prepared; they are anhydrous, and are yellow in colour. Of the salts of the second acid, the potassium salt, $[Fe(C_2O_4)_2H_2O,Cl]K_2$, and the pyridine salt, $[Fe(C_2O_4)_2H_2O,Cl]H_2,2C_5H_6N,H_2O$, are green in colour, and the guanidine salt, $[Fe(C_2O_4)_2H_2O,Cl]H_2,2CH_5N_3$, is yellow. The secondary and tertiary pyridine salts of the third acid were prepared, the former having $1H_2O$, the latter being anhydrous; they are orange to orange-yellow in colour. In water, the complex anions appear to break up into simple anions, since normal reactions are given with sodium acetate, silver nitrate, and ammonia.

The following sulphato-compounds were also prepared: *quinoline oxalato-sulphato-ferriate*, $[Fe(C_2O_4)SO_4]H,C_9H_7N,H_2O$, greyish-green, fine, narrow tablets; *dipyridine dioxalato-sulphato-ferriate*, $[Fe(C_2O_4)_2SO_4]H_3,2C_5H_5N$, yellowish-green, fine needles; *dipyridine-oxalato-disulphato-ferriate*, $[FeC_2O_4(SO_4)_2]H_3,2C_5H_5N$, yellow, fine, flat needles. Of these three salts, the quinoline salt is very sparingly soluble in water, the others are readily soluble. The former of the two pyridine salts can be recrystallised unchanged from water. A tertiary pyridine salt of this group could not be obtained.

The following oxalato-ferriates are described: *Tripyridine trioxalato-ferriate*, $[Fe(C_2O_4)_3]H_3,3C_5H_5N,3H_2O$, large, thick, six-sided emerald-green plates. This also crystallises with $\frac{1}{2}H_2C_2O_4$ instead of $3H_2O$ in yellowish-green leaves.

Diquinoline trioxalato-ferriate, $[Fe(C_2O_4)_3]H_3,2C_9H_7N,9H_2O$, long, fine, greenish-yellow needles, pointed at both ends.

Pyridine diaquodioxalato-ferriate, $[Fe(C_2O_4)_2(H_2O)_2]H,C_5H_5N$, yellowish-green, granular crystal aggregates. This also crystallises with $\frac{1}{2}H_2O$ in fine needles.

Quinoline diaquodioxalato-ferriate, $[Fe(C_2O_4)_2(H_2O)_2]H,C_9H_7N,H_2O$, fine, greenish-yellow powder.

Attempts to prepare corresponding malonic acid derivatives containing chlorine in the complex anion were unsuccessful, but the following new salts were prepared:

Pyridine dimalonato-diaquoferriate,

$$[Fe(CH_2C_2O_4)_2(H_2O)_2]H,C_5H_5N,2H_2O,$$

well formed, rhombohedral, almost colourless crystals, sparingly soluble in water; *quinoline dimalonato-diaquoferriate*, anhydrous, pale green, short needles, fairly soluble in water, from which it can be recrystallised; *guanidine dimalonato-diaquoferriate*, crystallising with $1H_2O$, microscopic, pale green needles, recrystallisable from water.

Chloro-oxalato- or chloro-malonato-compounds containing ferrous iron could not be prepared. A ferrous compound from pyridine and malonic acid was prepared, however, which appeared to be a non-electrolyte, and probably has the structure

$$\left[CH_2{<}\begin{matrix}CO\cdot O\\CO\cdot O\end{matrix}{>}Fe{<}\begin{matrix}C_5H_5N\\H_2O\end{matrix}\right].$$

It forms a yellow, crystalline powder and cannot be recrystallised from water. E. H. R.

The Sodium and Ammonium Molybdomalates. E. DARMOIS (*Compt. rend.*, 1921, **172**, 1486—1487. Compare A., 1920, ii, 575).—Measurements of the rotatory power of malic acid in the presence of varying amounts of ammonia and molybdic acid show that the crystalline ammonium molybdomalate obtained from mixtures of ammonium molybdate and malic acid or molybdic acid and ammonium malate contains molybdic acid, malic acid, and ammonia in the molecular proportions of 2 : 1 : 2. Sodium molybdomalate, similarly prepared, has a similar constitution. W. G.

Stereochemical Studies. V. Stereochemistry of Dichlorosuccinic Acid. BROR HOLMBERG (*Arkiv Kem. Min. Geol.*, 1921, **8**, No. 2, 1—35).—The author has previously shown (A., 1913, i, 7) that *r*-dichlorosuccinic acid, m. p. 175°, is resolvable into its optically active components, and has now characterised the active forms more minutely and also investigated more closely the meso- and racemic acids, especially as regards their decomposition products.

The *meso*-acid, m. p. 217—218° (decomp.), forms an anhydrous *potassium hydrogen* salt; the i-α-*phenylethylamine hydrogen* salt, m. p. 133—134°, d-α-*phenylethylamine hydrogen* salt, m. p. 128—129°, and l-α-*phenylethylamine hydrogen* salt, m. p. 128—129°, were prepared. When heated in a solution which is at first neutral and is gradually neutralised with alkali hydroxide, the acid decomposes in accordance with the equations: $(CO_2K{\cdot}CHCl)_2+2H_2O=[CO_2H{\cdot}CH(OH)]_2+2KCl$ and $(CO_2K{\cdot}CHCl)_2+H_2O=CH_3{\cdot}CHO+2CO_2+2KCl$; the dihydroxysuccinic acid formed is mostly of the meso-modification. In acid solution, *meso*-dichlorosuccinic acid decomposes into chlorofumaric and chloromaleic acids and in alkaline solution into chlorofumaric acid.

The racemic acid, m. p. 174—175° (decomp.), forms a *potassium* ($+H_2O$) and a *potassium hydrogen* salt ($+2H_2O$); the i-α-*phenylethylamine hydrogen* salt, m. p. 149—150°, methyl ester, m. p. 42—43° (compare Darzens and Sejourné, A., 1912, i, 535), and *ethyl* ester, which is a liquid losing hydrogen chloride on distillation, were prepared. In approximately neutral solution, the acid decomposes with formation principally of tartaric acid, together with carbon dioxide and acetaldehyde; in acid or alkaline solution, only chlorofumaric acid is formed.

The racemic acid may be resolved into its optically active components by means of optically active α-phenylethylamine. *d*-Dichlorosuccinic acid, m. p. 166—167° (frothing), has $[\alpha]_D^{19}+1{\cdot}1°$ (in water) and $-2{\cdot}3°$ (in *N*-hydrochloric acid); its *potassium hydrogen* salt, $[\alpha]_D^{19}+14{\cdot}8°$, and its *normal potassium* salt, $[\alpha]_D^{19}+11{\cdot}8°$, are anhydrous; the *d*-α-phenylethylamine hydrogen salt, m. p. 149—150°, l-α-*phenylethylamine hydrogen* salt, m. p. 136—137°, and the liquid *ethyl* ester, d_4^{20} 1·239, $[\alpha]_D^{20}+55°$. Treatment of the acid with ammonia in presence of ammonium chloride yields only chlorofumaric acid, whilst when the sodium salt is heated in presence

of silver nitrate, carbon dioxide, acetaldehyde, mesotartaric acid, and small proportions of racemic and *l*-tartaric acids are formed.

l-Dichlorosuccinic acid, m. p. 166—167° (decomp.), has $[\alpha]_D^{19}$ −79·5° (in ethyl acetate), −71·0° (in alcohol), −63·5° (in acetone), and −2·1° (in water); the d-*α-phenylethylamine hydrogen* salt, m. p. 147—148°, and the *methyl* ester (probably racemised to some extent), m. p. 64—65·5°, $[\alpha]_D^{17}$ −68·4°, were prepared. In approximately neutral solution, the acid decomposes, giving chiefly *d*-tartaric acid, together with carbon dioxide and acetaldehyde.

T. H. P.

The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. II. Products derived from α-Halogenated Adipic Acids. CHRISTOPHER KELK INGOLD (T., 1921, **119**, 951—970).

Preparation of Derivatives of Cholic Acid. J. D. RIEDEL (D.R.-P. 334553; from *Chem. Zentr.*, 1921, ii, 1020).—Esters of cholic acid are treated with dehydrating agents. The products thus obtained are saponified and by subsequently acidifying the free acids are obtained. For example, *methyl cholate* is heated with glycollic acid and potassium hydrogen sulphate at 130°. From the mixture of unsaturated acids, apo*cholic acid* is obtained as a compound, with acetic acid, $C_{24}H_{38}O_4,CH_3{\cdot}CO_2H$, forming needles, m. p. 150—160° (after sintering). After removal of the acetic acid, the *apo*cholic acid is almost tasteless. From the acetic acid mother-liquors, other unsaturated bile acids are precipitated by water; these are distinguished from *apo*cholic acid by their greater solubility in ordinary organic solvents. Aqueous solutions of the salts have a strong solvent action on many insoluble substances.

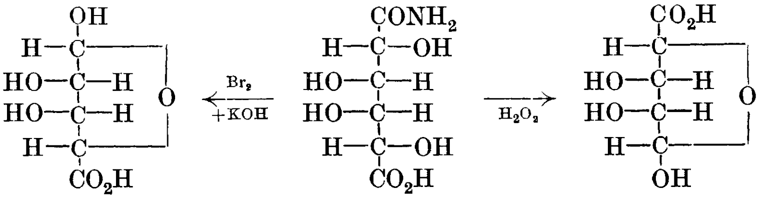
G. W. R.

A Method of Preparation of Succinylsuccinic Ester. M. SOMMELET and P. COUROUX (*Bull. Soc. chim.*, 1921, [iv], **29**, 402—406).—Ethyl γ-chloroacetoacetate reacts with sodium ethoxide or sodium phenoxide to give ethyl succinylsuccinate, m. p. 126—127°, together with accessory products not characterised. W. G.

Action of Ammonium Citrate on Alkaline-earth Sulphates. (MLLE) VIRGINIE TEODOSSIU (*Bull. Soc. Chim. România*, 1921, **3**, 9—17).—The reaction between ammonium citrate solution and calcium sulphate, strontium sulphate, and barium sulphate is directly proportional to the solubility of the sulphate in water and inversely proportional to the molecular weight of the metal. At 20°, the maximum reaction is attained by using a 0·2 mol. per litre ammonium citrate solution; in three hours, 50% of the calcium sulphate, 12% of the strontium sulphate, or about 3% of the barium sulphate present is converted into citrate. W. P. S.

Oxidative Degradation of Mucic and Saccharic Acids to New Aldehyde-acids of the Sugar Series. M. BERGMANN (*Ber.*, 1921, **54**, [*B*], 1362—1380).—The degradation of the semiamide of mucic acid is effected in either of two manners: (1) by

means of hydrogen peroxide, which leaves the carboxylamido-group mainly unaffected and passes through the stages: mucic acid semi-amide ⟶ [lyxuronamide] ⟶ lyxuronamide tetra-acetate ⟶ osimine of lyxuronamide ⟶ lyxuronic acid, and (2) with sodium hypobromite, whereby oxidation is effected at the amide end of the chain and the carboxy-group is left mainly untouched. The two processes yield the same lyxuronic acid when applied to optically inactive mucic acid, but enantiomorphous lyxuronic acids when applied to the active substance, as would be expected according to the scheme:



d-Lyxuronic acid. *d*-Mucic-semiamide. *l*-Lyxuronic acid.

The *semiamide* of mucic acid, microscopic, four-sided plates, decomp. 192°, after darkening at about 175°, is prepared by the action of concentrated aqueous ammonia on mucic acid lactone; the salts are generally sparingly soluble in water, the crystalline *sodium*, *ammonium*, *barium*, and *calcium*, and the *lead* and *silver* compounds being described. The *brucine* and *cinchonine* salts crystallise well, but are unsuitable for the resolution of the amide acid. The latter is therefore transformed into the *penta-acetate*, four-sided plates ($+H_2O$), decomp. about 197° (corr.), after slight softening, which is resolved by crystallisation of the brucine salt from absolute alcohol, in which the *salt* of the *d*-acid, $[\alpha]_D^{20}$ −29·8° to −30·0°, is the more sparingly soluble. The latter is decomposed by ammonia with simultaneous removal of the five acetyl groups, thus giving d-*mucic-semiamide*, a colourless, heavy powder which in its solubility closely resembles the *dl*-form, $[\alpha]_D^{17}$ +23·6 to +23·95°, as the ammonium salt in aqueous solution.

The degradation of the *dl*-semiamide is effected by the addition of acetic acid, iron acetate, ferrous sulphate, and concentrated hydrogen peroxide to an aqueous solution of the sodium salt, the temperature being regulated in such a manner as not to exceed 55°. The yields are invariably poor, and the operations are sometimes unsuccessful for some unexplained reason. The direct isolation of lyxuronamide from the products of the reaction is impracticable, and the substance is therefore transformed by direct acetylation of the crude material into the corresponding *tetra-acetate*, microscopic, colourless needles or prisms, m. p. about 217° (corr.) after softening at 170°. The latter is transformed by methyl-alcoholic ammonia into the *osimine* of *lyxuronamide*,

$$\underbrace{NH_2\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CO\cdot NH_2;$$

this appears to be contaminated with small amounts of lyxuronamide which either cannot be removed or are persistently re-

formed, but yields a homogeneous *hydrochloride*, hexagonal plates or prisms, m. p. about 158° (decomp.), after darkening at 140°, and *sulphate*, hexagonal leaflets. dl-*Lyxuronic acid* is readily prepared from the amide-acetate or osimine by the action of warm dilute mineral acids, but the isolation of the acid itself or of a crystalline salt has not yet been effected. It reduces Fehling's and ammoniacal silver solution strongly in hot solution, is decomposed by alkali with the formation of yellow or brown solutions, and by concentrated mineral acids with the production of humus-like substances. It does not exhibit very characteristically the usual colour reactions of glycuronic acid and allied substances. Its identity is established by means of the following derivatives: *phenylhydrazine salt* of *lyxuronic acid phenylosazone*, pale yellow needles, m. p. about 164° (decomp.), when rapidly heated; *lyxuronic acid phenylosazone*, microscopic needles, m. p. about 170° (corr. decomp.); as-*phenylbenzylhydrazine* salt of *lyxuronic acid phenylbenzylhydrazone*, almost colourless, microscopic needles ($+H_2O$), m. p. about 88—89°, *compound* with *p*-bromophenylhydrazone, $C_{17}H_{18}O_5N_4Br_2$, a lustrous, yellow, crystalline powder, decomp. 204° after becoming discoloured at 200°.

The semiamide of sodium *dl*-mucate is readily converted by the addition of potassium hydroxide and bromine to its aqueous solution into *dl*-lyxuronic acid, which is identified by the hydrazine derivatives just described.

Similar experiments, starting from the semiamide of *d*-mucic acid, are also described. In this instance, the isolation of a tetra-acetate from the product of the action of hydrogen peroxide could not be effected, and the crude product was therefore successively converted into the as-*phenylbenzylhydrazone*, the free *aldehyde acid*, and the *phenylosazone* of the latter, which was found to be lævorotatory when dissolved in a mixture of pyridine and alcohol. The similar compound prepared by means of bromine and potassium hydroxide from the semiamide of *d*-mucic acid was dextrorotatory and slightly less active, showing admixture with the racemic substance, owing to the fact that the process of degradation did not affect the carboxylamide group exclusively.

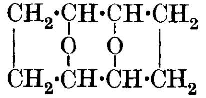
Potassium saccharate is readily oxidised by hydrogen peroxide in the presence of acetic acid and iron salts, and by the action of phenylhydrazine on the crude product, it has been found possible to isolate the phenylhydrazine salt of *d*-lyxuronic acid phenylosazone, decomp. about 164°.

[With W. W. Wolff.]—The *semiamide* of *saccharic acid*, colourless needles, m. p. about 135° (decomp.), when rapidly heated, $[\alpha]_D^{19}+22{\cdot}5°$ in aqueous solution, is prepared by the action of concentrated aqueous ammonia on the corresponding lactone.

H. W.

The Condensation of Formaldehyde with Acetone. Arno Müller (*Ber.*, 1921, **54**, [*B*], 1142—1148).—The condensation of formaldehyde with acetone in the presence of a considerable quantity of alkali has been examined previously by Werner (P.,

1904, **20**, 196), who isolated an amorphous substance to which he ascribed the formula, C_4H_5O. The substance has now been prepared as a yellowish-orange powder which becomes carbonised above 300°; analyses and determinations of molecular weight in freezing glacial acetic acid solution indicate the formula $C_8H_{12}O_2$. It does not yield a phenylhydrazone or an oxime under the usual conditions. Oxidation with potassium permanganate in alkaline solution gives carbon dioxide and a mixture of fatty acids in which the presence of acetic acid is definitely established. Treatment with nitric acid yields the *dinitro*-derivative, $C_8H_8O_2(NO_2)_2$, a pale orange-brown powder, m. p. 65—68°, decomp. 82—85° (the *sodium* and *iron* salts are described). Treatment of the substance dissolved in boiling glacial acetic acid with bromine leads to the formation of the compound $C_8H_8O_2Br_2$, a chocolate-brown powder from which the halogen is largely removed by treatment with quinoline at 125—130°. The properties and mode of formation of the substance are considered to be in harmony with the annexed formula. H. W.



Preparation of Acetaldehyde from Acetylene and Steam. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT VORM. RÖSSLER (D.R.-P. 334357; from *Chem. Zentr.*, 1921, ii, 1019).—In the preparation of acetaldehyde by the interaction of acetylene and steam at high temperature in the presence of oxides or mixtures of oxides, the materials thus used as catalysts may become inactive. Their activity may be restored by the passage of a current of air, also at high temperature. The effect of this treatment is either to oxidise carbon deposited on the catalyst or else to restore the partly reduced metallic oxides to their original state of oxidation. Large quantities of acetaldehyde may thus be prepared from acetylene, using only small quantities of catalyst. An example is given of the use as a catalyst of molybdic acid deposited on asbestos. G. W. R.

Elimination of Carbon Dioxide from Organic Compounds. IV. Fission of Chloral Hydrate by Mercury Acetate, Mercury Oxide, and certain other Metallic Oxides. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. Deut. pharm. Ges.*, 1921, **31**, 233—239. Compare A., 1920, i, 312).—The action of magnesium oxide and of the oxides of mercury, zinc, and copper on chloral hydrate resembles that of the alkali and alkaline earth hydroxides in so far as chloroform is produced independently of the chemical character of the metallic ion used. It differs, however, in that the formic acid simultaneously formed is retained as formate when the alkali or alkaline earth hydroxides are used, whereas it is further decomposed to carbon monoxide and carbon dioxide under the influence of magnesium oxide or the oxides of the heavy metals; this is particularly the case with mercuric oxide. With the metallic oxides, also, a portion of the chloroform is decomposed with production of chloridion. The main reaction with mercuric oxide is

expressed by the scheme $2CCl_3{\cdot}CH(OH)_2+8HgO=HgOCl,5HgCl+2H{\cdot}CO_2Hg+2CO_2+H_2O$; subsidiary reactions occur in accordance with the equations, $2CCl_3{\cdot}CH(OH)_2+HgO=(H{\cdot}CO_2)_2Hg+2CHCl_3+H_2O$; $2(H{\cdot}CO_2)_2Hg=2H{\cdot}CO_2Hg+CO_2+CO+H_2O$; $2H{\cdot}CO_2Hg=2Hg+CO+CO_2+H_2O$. H. W.

Action of Alkalis on Glyoxal. B. HOMOLKA (*Ber.*, 1921, **54**, [*B*], 1393—1396).—If an aqueous solution of glyoxal, or preferably of its sodium hydrogen sulphite compound, is treated with an excess of sodium carbonate solution, it becomes, slowly in the cold, but more rapidly when warm, dark yellow in colour, owing to the absorption of atmospheric oxygen, and ultimately deposits bluish-black crystals of the sodium salt of tetrahydroxy-*p*-benzoquinone. The same compound, together with rhodizonic acid, croconic acid, and much glycollic acid, is formed in the presence of sodium hydroxide. The observations are of peculiar interest as indicating an inversion of Harries's fission of benzenetriozonide into glyoxal, leading to a ready method of preparing aromatic compounds which are otherwise difficultly accessible and showing a possible mode of production of aromatic substances from simple materials and under gentle conditions in plants.

Rhodizonic acid is also produced by the action of normal sodium sulphite on an aqueous solution of glyoxal, or, in poorer yield, on a solution of sodium dihydroxytartrate. H. W.

Researches on Residual Affinity and Co-ordination. V. Gallium Acetylacetone and its Analogues. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW (T., 1921, **119**, 1058—1066).

The Influence of Ammonium Molybdate on the Rotatory Power of Mannitol. GEORGES TANRET (*Compt. rend.*, 1921, **172**, 1500—1503).—When 15 grams of mannitol and 30 grams of ammonium molybdate are dissolved in 200 c.c. of water, the solution soon yields a crystalline *compound* having the composition $[(13MoO_3,7NH_3,7C_6H_{14}O_6)-6H_2O]3H_2O$. This substance is acid to indicators and very unstable. In aqueous solution it has $[\alpha]_D$ $+52{\cdot}5°$ for concentrations varying from 1 in 20 to 1 in 60. It is immediately decomposed by alkalis with total loss of rotatory power. Mineral acids decompose it in the cold, and an equilibrium is established varying with the weight of acid used, the rotatory power diminishing as the concentration of the acid increases. W. G.

A New Form of Galactosephenylmethylhydrazone. ÉMILE VOTOČEK (*Bull. Soc. chim.*, 1921, [iv], **29**, 406—409).—Galactosephenylmethylhydrazone crystallises from 96% alcohol in the form of white scales, which are clinorhombic. They are anhydrous. Crystallised from boiling water, the hydrazone is obtained as pale yellow, silky, orthorhombic needles containing $1H_2O$. W. G.

Lævulosan. AMÉ PICTET and JOSEPH REILLY (*Helv. Chim. Acta*, 1921, **4**, 613—616).—Considerable discrepancy exists between

the properties of the various substances described in the literature as lævulosan. The authors have therefore prepared the substance by heating dried lævulose at 15—20 mm. pressure at 115—120° during two to three hours, washing the product rapidly with ethyl alcohol, and solution of the residue in methyl alcohol followed by precipitation with ether. After being dried in a vacuum at 100°, lævulosan, $C_6H_{10}O_5$, forms a white, very hygroscopic powder, m. p. about 150°, $[\alpha]_D^{20}$ +18·6° in aqueous, +19·5° in methyl-alcoholic solution. It is not fermented by brewer's yeast. Its reducing power towards Fehling's solution is exactly one-third of that of lævulose. It is readily converted into the latter by boiling water. When heated with phenylhydrazine in glacial acetic acid solution, it gives phenylglucosazone, m. p. 206—207°. With hydrochloric acid, it yields a crystalline *chloro*-derivative. It is too early at present to assign a constitutional formula to the substance, but the presence in it of three hydroxyl groups is demonstrated by the preparation of the trinitrate, m. p. 139—140°, *triacetate*, m. p. 85°, and *tribenzoate*, small, rectangular plates, m. p. 125—126°. H. W.

Inulin. HANS PRINGSHEIM and ALEXANDER ARONOWSKY (*Ber.*, 1921, **54**, [*B*], 1281—1286).—The action of a hot mixture of acetic anhydride and pyridine, which proceeds spontaneously after being started, leads to the formation of *triacetylinulin*, lustrous crystals, m. p. 102—103°, after softening at 95°, $[\alpha]_D^{20}$ −42·55°, in glacial acetic acid solution. The mean molecular weight of the compound in naphthalene, glacial acetic acid, and phenol respectively is **2633,** which corresponds most closely with the presence of nine lævulose residues in the molecule and is thus in excellent agreement with the recent observations of Karrer and Lang on methylated inulins (this vol., i, 312). When hydrolysed with ice-cold alcoholic potassium hydroxide solution, it regenerates inulin, the identity of which with the original material is confirmed by comparison of the chemical and physical properties, specific rotations, and Röntgen measurements according to Debye-Scherer. H. W.

Cellulose and its Esters. II. Stability and Viscosity of Cellulose Nitrates. J. DUCLAUX (*Bull. Soc. chim.*, 1921, [iv], **29**, 374—382. Compare A., 1920, i, 534).—In confirmation of Fric's work (A., 1912, i, 73), it is shown that the diminution in the viscosity of solutions of a cellulose nitrate as the temperature to which the cellulose nitrate is heated increases is quite general. There is a definite relationship between the diminution in viscosity and loss of weight of the cellulose nitrate, and one figure may be calculated from the other. Such viscosity measurements, therefore, furnish a ready means of following the degradation of a cellulose nitrate by heating, and a method of determining its stability. W. G.

The Distillation of Methylcelluloses under Reduced Pressure. JOSEPH REILLY (*Helv. Chim. Acta*, 1921, **4**, 616—621).—In view of the discordance of the results obtained by Pictet and Sarasin (A., 1918, i, 59) by the distillation of cellulose and by Hess

and Wittelsbach (A., 1920, i, 532) in the similar treatment of ethylcellulose, the author has examined the behaviour of a series of methylated celluloses (compare Woodhouse and Denham, T., 1913, **103**, 1735; 1914, **105**, 2357; 1921, **119**, 80) containing 25·3%, 28·1%, 33·4%, and 43·7% of methoxyl and thus corresponding approximately with dimethyl- and trimethyl-cellulose. The most definite results are obtained with the second product, which, when distilled under 10—15 mm. pressure, yields 50% of a product composed entirely of methylated derivatives, the most volatile portion of which, after suitable purification, has the composition of a dimethyllævoglucosan and is hydrolysed to a dimethylglucose, thus confirming Pictet and Sarasin's conception of the existence of the lævoglucosan group in the cellulose molecule.

The gaseous products from the fourth preparation contain carbon dioxide (43·4%), carbon monoxide (28·9%), oxygen (0·15%), unsaturated hydrocarbons (3·1%), and saturated hydrocarbons [methane], 23·2%. H. W.

Lignin derived from Rye-straw. ERNST BECKMANN, OTTO LIESCHE, and FRITZ LEHMANN (*Zeitsch. angew. Chem.*, 1921, **34**, 285—288).—The most suitable method for extracting lignin consists in digesting straw with a mixture of 96% alcohol and 2% sodium hydroxide, after which the solution is neutralised with hydrochloric acid, the alcohol distilled off, and the product freed from hexosan and pentosan by treatment with hydrochloric acid. Divergences in regard to the formula for lignin may be due to the various methods applied for its extraction, as well as to secondary changes in the product. The authors consider that its composition is most nearly represented by the formula $C_{40}H_{46}O_{15}$. W. J. W.

Methylammonium Iodide. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1921, **423**, 300. Compare this vol., i, 606–618).—Methylammonium iodide is occasionally encountered in the course of experiments on the action of hydriodic acid on methylated uric acid derivatives. It forms nearly rectangular tables, m. p. 263—265° (corr.), decomp., that is, considerably higher than recorded by Dunstan and Goulding (T., 1897, **71**, 579). C. K. I.

Separation of β-Aminoethyl Alcohol from Mixtures containing Choline. E. FOURNEAU and A. GONZÁLEZ (*Anal. Fís. Quím.*, 1921, **19**, 151—155).—Among the products of the hydrolysis of lipoids, β-aminoethyl alcohol is obtained mixed with a large excess of choline. By treatment with naphthalene-β-sulphonyl chloride in ethereal solution, extracting with sodium hydroxide solution, and acidifying with dilute hydrochloric acid, naphthalene-β-sulphonyl-β-aminoethyl alcohol is precipitated and may be recrystallised from boiling toluene. G. W. R.

Viscosities of Solutions of Amino-acids. GUNNAR HEDESTRAND (*Arkiv Kem. Min. Geol.*, 1921, **8**, No. 5, 1—9).—The author has measured the viscosities at 18° of 2*N*-, *N*- (also at 40°), and 0·4*N*- (also at 40°) glycine, 0·25*N*-alanine, and 0·03*N*-*m*-amino-

benzoic acid solutions containing varying proportions of acid or alkali. With glycine solutions, the viscosity exhibits a minimal value for $p_H = 6{\cdot}4$, whereas for the isoelectric point the calculated value of p_H is 6·6; for alanine, the corresponding values of p_H are 6·4 and 6·7, and for *m*-aminobenzoic acid 3·8 and 3·1. The curves connecting viscosity with p_H are steeper on the alkaline than on the acid side of the isoelectric point. T. H. P.

The Influence of the Structure and Configuration of Substrates (Polypeptides) on Ferment Action. EMIL ABDERHALDEN and HANS HANDOVSKY (*Fermentforsch.*, 1921, **4**, 316—326).—*Glycyl*-d-*leucylglycyl*-l-*leucine*, m. p. 225·5° (corr.), $[\alpha]_D^{20} + 16{\cdot}6°$ in water, was prepared by the usual methods with the object of determining whether ferments hydrolyse polypeptides which contain as one unit the enantiomorph of a naturally occurring amino-acid, the remaining units being those occurring naturally. As intermediate products, the following compounds were prepared: α-*bromo*-l-iso*hexoylglycyl*-l-*leucine*, hygroscopic crystals, m. p. 167° (corr.), $[\alpha]_D^{20} - 27{\cdot}2$ in absolute alcohol; d-*leucylglycyl*-l-*leucine*, decomposes at 269° (corr.), $[\alpha]_D^{20} - 18{\cdot}8°$ in 10% ammonia; *chloroacetyl*-d-*leucylglycyl*-l-*leucine*, amorphous powder, which melts at 103·5° (corr.) after sintering between 72° and 74° (corr.), $[\alpha]_D^{20} + 9{\cdot}3$ in absolute alcohol.

Whilst glycyl-*l*-leucine and glycyl-*l*-leucylglycyl-*l*-leucine are hydrolysed by yeast maceration juice, glycyl-*d*-leucine and glycyl-*d*-leucylglycyl-*l*-leucine, which both contain the non-natural *d*-leucyl unit, are unattacked by this ferment. In the latter case, evidence was obtained of a combination with the ferment, from which it is concluded that it is not the combination substrate+ferment, but the actual hydrolysis itself, which is specific. E. S.

The Cleavage, by Ferments, of Polypeptides containing Amino-acids which have not yet been found as Cleavage Products of Proteins. EMIL ABDERHALDEN and H. KÜRTEN (*Fermentforsch.*, 1921, **4**, 327—337).—The investigation was undertaken to determine whether polypeptides containing as units hitherto unknown amino-acids could be hydrolysed by ferments.

d-l-α-*Amino*-n-*valeric acid*, $CH_2Me{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, to which the name *norvaline* is given, is prepared by the usual methods from *n*-valeric acid. It forms microscopic leaflets, m. p. 303° (corr.). Resolution is effected by fractional crystallisation of the brucine salt of the formyl derivative and subsequent hydrolysis, giving d-*norvaline* (sinters at about 305°, $[\alpha]_D^{20} + 23{\cdot}0°$ in 20% HCl) and l-*norvaline* (sinters at about 307°, $[\alpha]_D^{20} - 24{\cdot}2°$ in 20% HCl). The copper salts are sparingly soluble in water. The following are the derivatives prepared: *phenylcarbamido*-d-*norvaline*, prisms, sintering at about 137° (corr.); *phenylcarbamido*-l-*norvaline*, sinters at about 137° (corr.); *phenylcarbamido*-d-l-*norvaline*, prisms, sintering at about 164° (corr.); *formyl*-d-l-*norvaline*, platelets, m. p. 130° (corr.); *formyl*-d-*norvaline*, m. p. 137°, $[\alpha]_D^{18} + 2{\cdot}05°$ in *N*-hydrochloric acid; *formyl*-l-*norvaline*, m. p. 132° (corr.), $[\alpha]_D^{18} - 2{\cdot}10°$ in

absolute alcohol; *chloroacetyl*-d-*norvaline*, prisms, m. p. 107° (corr.); *chloroacetyl*-l-*norvaline*, m. p. 108° (corr.); *glycyl*-d-*norvaline*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CHPr\cdot CO_2H$, microscopic prisms, sinters at about 223° (corr.), $[\alpha]_D^{20} -10\cdot17°$ in *N*-hydrochloric acid; *glycyl*-l-*norvaline*, microscopic prisms, sinters at about 220° (corr.), $[\alpha]_D^{20} +10\cdot28°$ in *N*HCl.

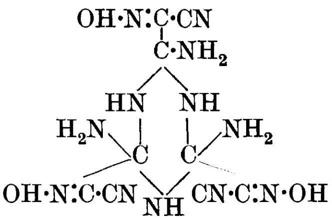
Fermentation experiments show that whilst glycyl-*d*-norvaline is hydrolysed by yeast maceration juice, glycyl-*l*-norvaline is unattacked. The possibility of the natural occurrence of *d*-norvaline is therefore not excluded. E. S.

Local Anæsthetics. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1921, [iv], **29**, 413—416).—Dichlorohydroxy*iso*butyric acid gives an *ethyl* ester, b. p. 112°/13 mm., which, when heated with dimethylamine hydrochloride for six hours at 110°, gives *ethyl tetramethyldiaminohydroxy*iso*butyrate*, b. p. 115°/12 mm., which yields a *benzoyl* derivative in the form of its *hydrochloride*, m. p. 155°. This is not neutral, and when tried as a local anæsthetic on the eyelid was found to have an irritant action. *Ethyl tetraethyldiaminohydroxy*iso*butyrate* has b. p. 158°/22 mm. When dichlorohydroxy*iso*butyric acid is dissolved in aqueous ammonia and the solution saturated with ammonia, a *compound*, m. p. 214°, is obtained, which is probably iminobisaminohydroxy*iso*butyric acid hydrochloride. W. G.

Use of Chemically Precipitated Iron in the Synthetic Production of Alkali Cyanide. RYÔSABURÔ HARA (*Tech. Rep. Tôhoku Imp. Univ.*, 1921, **2**, (1)).—As a substitute for mechanically divided iron as catalyst, charcoal saturated with iron chloride has proved effective, and a material saving of reduced iron is gained. A still more efficient catalyst is obtained by treatment of the "ironised charcoal" with steam, whereby iron oxide is precipitated. Comparative yields of cyanide obtained by the use of metallic iron, iron chloride, and iron oxide were 79·8, 79·8, and 92·3% respectively. W. J. W.

Course of the Reaction between Malononitrile and Nitrous Acid. OTTO DIELS and ERICH BORGWARDT (*Ber.*, 1921, **54**, [*B*], 1334—1343).—Although oximinomalonic acid and ethyl oximinocyanacetate are well known substances, the corresponding compounds from malononitrile do not appear to have been described; this is probably due to the fact that reaction between nitrous acid and the nitrile takes a somewhat complicated course, leading in the first instance mainly to the *substance* $OH\cdot N:C(CN)\cdot C(OEt)(OH)\cdot NH_2$, which, however, readily undergoes further change. It is prepared by the addition of a solution of sodium in alcohol to an alcoholic solution of malononitrile and amyl nitrite at 0° and subsequent cautious acidification of the *sodio*-compound with acetic acid; it crystallises in long, yellow prisms, decomp. about 110°, after darkening at 90°, which gradually become orange-red when preserved in a vacuum over phosphoric oxide. With warm hydrochloric acid (*d* 1·19), it yields ammonium chloride and ethyl oximino-

cyanoacetate, colourless prisms, m. p. 129°. When treated with boiling alcohol, it gives a mixture of a *substance*, $C_9H_{12}O_3N_{12}$ (probably annexed formula), characteristic minute, yellow crystals, decomp. about 321°, after darkening above 240°, and a more readily soluble *product*, NH[C(OH)(OEt)·C(CN):NOH]$_2$, almost colourless prisms, m. p. 153·5° (decomp.) after softening at 152°, which is transformed by aqueous ammonia into ammonium oximinocyanoacetate, m. p. 145°, and by fuming hydrochloric acid into ethyl oximinocyanoacetate.



The substance $C_5H_9O_3N_3$ (see above) is converted by ammonia into a mixture of the compound $C_9H_{12}O_3N_{12}$ and the *product* NH[C(OH)(NH$_2$)·C(CN):N·OH]$_2$, pale yellow crystals, m. p. 198° (decomp.); the latter is transformed by concentrated hydrochloric acid into oximinocyanoacetamide, m. p. 183° (decomp.).

The substance $C_9H_{12}O_3N_{12}$ is converted by warm dilute sulphuric acid into the sulphate, $C_9H_{12}O_3N_{12},1{\cdot}5H_2SO_4,1{\cdot}5H_2O$, colourless needles, m. p. 203—204° (from which the original compound is readily regenerated by the action of alkali), and by concentrated hydrochloric acid into ammonium chloride and the *hydrochloride*, $C_9H_{11}O_4N_{11},3HCl$, colourless crystals, m. p. about 195° (decomp.), after darkening at about 180°, from which alkali liberates the *substance* $C_9H_{11}O_4N_{11}$, yellow octahedra, decomp. about 316°, after becoming brown at about 280°. Treatment with acetic anhydride gives the acetyl *derivative*, $C_7H_7O_4N_3$, coarse, transparent crystals, m. p. 122°, which is decomposed by water into acetic acid and the *substance* $C_5H_5O_3N_3$, colourless leaflets, m. p. 207°. Methyl sulphate converts the compound $C_9H_{12}O_3N_{12}$ into the methyl ether of oximinocyanoacetamide, m. p. 172°, after softening at 169°. Concentrated alkali hydroxide solutions decompose the substance $C_9H_{12}O_3N_{12}$ extensively yielding, amongst other compounds, oximinomalonamide (compare Tilden and Forster, T., 1895, **67**, 489; Whiteley, T., 1900, **77**, 1040). H. W.

Composition of Swedish Shale Oil. GUSTAF HELLSING (*Arkiv Kem. Min. Geol.*, 1920, **7**, No. 29, 1—23).—The author has investigated a sample of oil obtained from Swedish shale by direct heating and subsequent fractionation. The oil is poor in paraffin hydrocarbons, consists largely of naphthenes, and is far richer than Scottish or French shale oil in aromatic hydrocarbons, toluene, *p*-xylene, ψ-cumene, another trimethylbenzene (? hemimellithene), and durene being identified; naphthalene is present only in traces if at all. The aromatic constituents are regarded as primary distillation products and not as secondary products. T. H. P.

The Trichlorodinitrobenzenes; their Reaction with Sodium Methoxide and with Ammonia. E. J. E. HÜFFER (*Rec. trav. chim.*, 1921, **40**, 451—476).—The six trichlorodinitrobenzenes were

prepared as follows: 2 : 4 : 6-Trichloro-1 : 3-dinitrobenzene was obtained by the nitration of *s*-trichlorobenzene. 3 : 4 : 5-Trichloronitrobenzene when nitrated with a sulphuric–nitric acid mixture gave 3 : 4 : 5-*trichloro*-1 : 2-*dinitrobenzene*, m. p. 105—106°. 4 : 5 : 6-*Trichloro*-1 : 3-*dinitrobenzene*, m. p. 92—93°, was obtained by the direct nitration of 1 : 2 : 3-trichlorobenzene. 2 : 4 : 5-Trichloro-1 : 3-dinitrobenzene was obtained by nitration of 1 : 2 : 4-trichlorobenzene. 2 : 5-Dichloro-1 : 3-dinitrobenzene on reduction by titanium chloride yielded 2 : 5-*dichloro*-3-*nitroaniline*, m. p. 121—122°, giving an *acetyl* derivative, m. p. 175—176°, which when nitrated gave 2 : 5-*dichloro*-3 : 4-*dinitroacetanilide*, m. p. 170—171°, and this on hydrolysis yielded 2 : 5-*dichloro*-3 : 4-*dinitroaniline*, m. p. 195° (decomp.). In this aniline the amino-group was replaced by chlorine by the Sandmeyer reaction, giving 3 : 4 : 6-*trichloro*-1 : 2-*dinitrobenzene*, m. p. 70—71°. The yield of the last compound was very poor, the main bulk of the product being 2 : 3 : 5 : 6-tetrachloronitrobenzene, m. p. 98°. A better yield was obtained by direct nitration of 2 : 3 : 5-trichloronitrobenzene. 2 : 5-Dichloro-4-nitroaniline on chlorination gave 2 : 3 : 6-*trichloro*-4-*nitroaniline*, m. p. 145·5—146·5°, from which by diazotisation in the presence of nitric acid 2 : 3 : 5-*trichloro*-1 : 4-*dinitrobenzene*, m. p. 95—96°, was obtained. Attempts to prepare this compound by another way gave unexpected results, and another series of compounds as follows: 2 : 3 : 6-Trichloronitrobenzene was reduced by iron and hydrochloric acid, giving 2 : 3 : 6-*trichloroaniline*, m. p. 63—64°, which gave an *acetyl* derivative, m. p. 172—173°. This acetanilide on nitration yielded 2 : 3 : 6-*trichloro*-5-*nitroacetanilide*, m. p. 218—219°, which on hydrolysis gave 2 : 5 : 6-*trichloro*-3-*nitroaniline*, m. p. 111—112°, and in this the amino-group was replaced by a nitro-group as described above, 2 : 4 : 5-trichloro-1 : 3-dinitrobenzene, m. p. 102·5—103·5°, being obtained.

2 : 4 : 6-Trichloro-1 : 3-dinitrobenzene reacts vigorously with ammonia to give a *compound*, m. p. 265°, which is probably 5-chloro-4 : 6-dinitro-*m*-phenylenediamine. With sodium methoxide, it gives 3 : 5-*dichloro*-2 : 4-*dinitroanisole*, m. p. 148·5—149·5°, also obtained by the nitration of 3 : 5-dichloroanisole.

3 : 4 : 5-Trichloro-1 : 2-dinitrobenzene yields, with ammonia, 4 : 5 : 6-*trichloro*-2-*nitroaniline*, m. p. 138—139°, and with sodium methoxide, 4 : 5 : 6-*trichloro*-2-*nitroanisole*, m. p. 83°.

4 : 5 : 6-Trichloro-1 : 3-dinitrobenzene gives, with ammonia, 5 : 6-*dichloro*-2 : 4-*dinitroaniline*, m. p. 197—198°, and with sodium methoxide, 5 : 6-*dichloro*-2 : 4-*dinitroanisole*, m. p. 69—70°.

2 : 4 : 5-Trichloro-1 : 3-dinitrobenzene gives, with ammonia, 6-*chloro*-2 : 4-*dinitro*-m-*phenylenediamine*, m. p. 244—245°, and with sodium methoxide a mixture of 3 : 6-*dichloro*-2 : 4-*dinitroanisole* and 3 : 4-*dichloro*-2 : 6-*dinitroanisole*, or if excess of sodium methoxide is used the product is 6-*chloro*-2 : 4-*dinitro*-1 : 3-*dimethoxybenzene*, m. p. 70°.

3 : 4 : 6-Trichloro-1 : 2-dinitrobenzene gives, with ammonia, 3 : 5 : 6-*trichloro*-2-*nitroaniline*, m. p. 100—101°, and with sodium methoxide, 3 : 5 : 6-*trichloro*-2-*nitroanisole*, m. p. 55°, together with

some *dichlorodinitroanisole*, m. p. 138—140°, the constitution of which was not determined.

2 : 3 : 5-Trichloro-1 : 4-dinitrobenzene gives, with ammonia, 2 : 3 : 6-trichloro-4-nitroaniline, m. p. 145—146·5°, and with sodium methoxide, 2 : 3 : 6-*trichloro*-4-*nitroanisole*, m. p. 67·5°.

Quantitative measurements of the velocity of reaction with sodium methoxide show that the introduction of a second nitro-group into the trichloronitrobenzenes has considerably increased the value of the velocity constant, but not to such an extent as is the case with the chloronitro- and dichloronitro-benzenes. The introduction of a chlorine atom into the dichlorodinitro-benzenes has resulted in a diminution of the velocity constant. A grouping $Cl : NO_2 : Cl = 6 : 1 : 2$ results in general in a lowering of the velocity of substitution. W. G.

Aromatic Nitro-derivatives. XIV. A new Bromotrinitrobenzene. M. Giua (*Gazzetta*, 1921, **51**, i, 307—313.)—When heated with a mixture of fuming nitric and fuming sulphuric acids, 4-bromo-1 : 2-dinitrobenzene is converted mainly into 5-bromo-1 : 2 : 4-trinitrobenzene. The constitution of the latter is determined by its conversion into the methyl ether of 4 : 6-dinitroresorcinol by the action of excess of sodium methoxide. The same methyl ether is obtained when 5-chloro-1 : 2 : 4-trinitrobenzene (compare Nietzki and Zänker, A., 1904, i, 150) is treated with sodium methoxide in excess. By boiling alcoholic ammonia, 5-bromo-1 : 2 : 4-trinitrobenzene is transformed partly into 4 : 6-dinitro-1 : 3-diaminobenzene and partly into 5-bromo-2 : 4-dinitroaniline. The action of phenylhydrazine on 5-chloro-1 : 2 : 4-trinitrobenzene yields 5-chloro-2 : 4-dinitrohydrazobenzene and 4 : 6-dinitro-1 : 3-diphenylhydrazinobenzene.

5-*Bromo*-1 : 2 : 4-*trinitrobenzene*, $C_6H_2O_6N_3Br$, crystallises in needles, m. p. 120—121°, its alcoholic solution being coloured deep red and then yellow by addition of alkali. It is accompanied by a small proportion of a *compound*, m. p. 112—113°, which is possibly 4-bromo-1 : 2 : 3-trinitrobenzene.

5-*Bromo*-2 : 4-*dinitroaniline*, $C_6H_4O_4N_3Br$, forms yellow needles, m. p. 172—173°, and is possibly identical with the compound, m. p. 178·4°, obtained by Körner (A., 1876, i, 204) by the action of alcoholic ammonia on *m*-dibromodinitrobenzene; the latter is, therefore, probably 4 : 6-dibromo-1 : 3-dinitrobenzene.

4 : 6-*Dinitro*-1 : 3-*diphenylhydrazinobenzene*,

$$C_6H_2(NO_2)_2(NH\cdot NHPh)_2,$$

crystallises in orange-red prisms, m. p. 211—212° (decomp.), and gives a dark red coloration either with concentrated sulphuric acid or in alcoholic solution in presence of alkali.

5-*Chloro*-2 : 4-*dinitrohydrazobenzene*, $C_{12}H_9O_4N_4Cl$, forms reddish-yellow prisms, m. p. 165°, and decomposes at about 180°. T. H. P.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. III. The Partial Reduction of the Dinitrotoluenes by Stannous Chloride and Hydrochloric Acid. Harold Burton and James Kenner (T., 1921, **119**, 1047—1053).

Artificial "Saccharin" Substances. A. F. HOLLEMAN (*Rec. trav. chim.*, 1921, **40**, 446—450).—The benzene-*o*-disulphonamide described by Armstrong and Napper (P., 1900, **16**, 160) is considered by the author to be an ammonium salt of the imide, and to have the constitution $C_6H_4<^{SO_2}_{SO_2}>N\cdot NH_4,H_2O$. The corresponding *sodium* and *calcium* salts and the free *imide*, m. p. 192°, have been prepared. The imide is very soluble in water and its taste is both sweet and acid, leaving a bitter taste afterwards.

W. G.

Additive Reactions with Nitrous Gases. HEINRICH WIELAND (*Annalen*, 1921, **424**, 71—74).—It appeared from former work (A., 1903, i, 764; 1904, i, 54; 1905, i, 706) that whilst the addition of nitrogen trioxide to one of two conjugated double linkings led to the formation of a "ψ-nitrosite" (bisnitroso-nitro-compound, I) in which all the nitrogen atoms are directly attached to carbon, when the bond attacked was not in conjugation with another, the product was a "nitrosite" (bisnitroso-nitrite, II), that is, a substance containing nitrogen attached by means of oxygen to the remainder of the molecule. It would seem, however, in view of the work described in the accompanying papers (compare three abstracts immediately following), that this conclusion is incorrect, and that the primary additive product is in every case a substance in which all the entering nitrogen atoms have become attached to carbon, and it therefore should be classed as a ψ-nitrosite, although it may not invariably correspond exactly with the type represented by formula I.

$$\begin{array}{ll} \cdot\dot{C}\cdot\dot{C}\cdot NO_2 & \cdot\dot{C}\cdot\dot{C}\cdot O\cdot NO \\ \;| & \;| \\ N_2O_2 & N_2O_2 \\ \;| & \;| \\ \cdot\underset{\cdot}{C}\cdot\underset{\cdot}{C}\cdot NO_2 & \cdot\underset{\cdot}{C}\cdot\underset{\cdot}{C}\cdot O\cdot NO \\ \text{(I.)} & \text{(II.)} \end{array}$$

C. K. I.

The Union of Nitrogen Trioxide and Nitrogen Peroxide with Unsaturated Compounds. HEINRICH WIELAND and EWALD BLÜMICH (*Annalen*, 1921, **424**, 75—91).—The nature of the product obtained from stilbene by the action of nitrous gases (compare Schmidt, A., 1901, i, 266; 1902, i, 21) varies with the composition of the gas employed; if the gas be sufficiently rich in nitric oxide, stilbene-ψ-nitrosite (bis-α-nitroso-β-nitro-$\alpha\beta$-diphenylethane, formula annexed) alone is formed; if, on the other hand, the gas contains a large proportion of nitrogen peroxide, the product may consist solely of a mixture of the α- and β-forms of *s*-dinitrodiphenylethane.

$$\begin{array}{l} CHPh\cdot CHPh\cdot NO_2 \\ | \\ (NO)_2 \\ | \\ CHPh\cdot CH\cdot Ph(NO_2) \end{array}$$

Stilbene-ψ-nitrosite, m. p. 132° (decomp.), is decomposed by alcoholic potassium hydroxide with the elimination of hyponitrous acid and the formation of α-nitrostilbene. On boiling in organic solvents, such as chloroform, alcohol, and acetic acid, the whole of the nitrogen is eliminated as oxides and stilbene is regenerated. When acetic acid is employed, a considerable degree of recombination takes place between the stilbene and the eliminated nitrogen peroxide, and since the dinitrostilbenes so formed are stable under

the conditions employed, this accounts for the production of these substances observed by Schmidt and attributed by him to oxidation. The formation of benzaldehyde, also observed by Schmidt, is due to the occurrence of a side-reaction whereby the ψ-nitrosite is broken down into benzaldehyde, phenylnitromethane, and nitrous oxide :

$$N_2O_2(CHPh{\cdot}CHPh{\cdot}NO_2)_2+H_2O=2CHPhO+2CH_2Ph{\cdot}NO_2+N_2O.$$

β-*Nitro-α-acetoxy-αβ-diphenylethane*, yellow prisms, m. p. 99—100°, is another by-product.

[With F. REINDEL.]—The structure of the less fusible form of *s*-diphenyldinitroethane has been placed beyond question by synthesis from *phenylbromonitromethane.* This substance, a pale yellow oil, b. p. 131°/16 mm., 122°/10 mm., is produced along with a small amount of 3 : 4 : 5-triphenyl*iso*oxazole (Heim, A., 1911, i, 718) when the sodium compound of phenylnitromethane is treated with bromine–water, and on digesting with molecular silver is converted into *s*-diphenyldinitroethane.

*cyclo*Hexene-ψ-nitrosite (Baeyer, A., 1894, i, 175) also eliminates hyponitrous acid on boiling with alcoholic potassium hydroxide, the potassium salt of *aci*-2-nitro*cyclo*hexanol being produced. On treatment with mineral acids, this is converted into 1-nitro-Δ^1-*cyclo*hexene.

[With C. REISENEGGER.]—Naphthalene is the principal product of the action of nitrogen peroxide on Δ^1-dihydronaphthalene, naphthalene-2-diazonium nitrate being formed as a by-product.

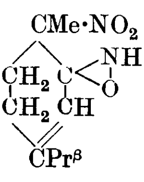
[With C. REISENEGGER.]—The sole product of the action of nitrogen peroxide on distyryl ketone under the usual experimental conditions is a dinitro-compound, *δε-dinitro-Δ^α-αε-diphenylpenten-γ-one* (formula below), m. p. 127—129° (decomp.), which undergoes hydrolysis with alkalis in two directions. With alcoholic ammonia, the principal products are benzaldehyde and styryl nitromethyl ketone, whilst with alcoholic potassium hydroxide they are β-nitro-α-phenylethylene and cinnamic acid :

$$NO_2{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CO{\cdot}CH{:}CHPh+H_2O=CHPh{\cdot}O+ \\ CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}NO_2+HNO_2;$$

$$NO_2{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CO{\cdot}CH{:}CHPh+H_2O=CHPh{:}CH{\cdot}NO_2+ \\ CHPh{:}CH{\cdot}CO_2H+HNO_2.$$

C. K. I.

Terpinene "Nitrosite." HEINRICH WIELAND and FRITZ REINDEL (*Annalen*, 1921, **424**, 92—99).—The additive product with nitrogen trioxide formed by α-terpinene ($\Delta^{1:3}$-dihydrocymene) (A., 1907, i, 943; 1908, i, 925; 1905, i, 603) eliminates about 25% of its nitrogen as ammonia when reduced by hydrogen in the presence of palladium black, the product being a mixture of a diamine and a monoamine. This fact, in conjunction with the molecular weight of the compound, points to its being 1-*nitro*-2-iso*oximino*-Δ^3-*tetrahydrocymene* (formula annexed), both nitrogen atoms being directly attached to carbon.



The monoamine and diamine formed by the reduction were partly separated by distillation in a good vacuum, but the monoamine (presumably 2-*aminohexahydrocymene*) could not be obtained in a pure condition. 1 : 2-*Diaminohexahydrocymene* was isolated as its *dibenzoyl* derivative, which separates from dilute alcohol in slender needles, m. p. 165°. The *monohydrochloride* of the diamine crystallises from alcohol in slender needles, m. p. 290° (decomp.).

C. K. I.

The Addition of the Higher Oxides of Nitrogen to the Triple Carbon Linking. HEINRICH WIELAND and EWALD BLÜMICH (*Annalen*, 1921, **424**, 100—107).—The authors have investigated the products obtained by the action of nitrogen peroxide on phenylacetylene and tolane.

Phenylacetylene yields $\alpha\beta$-*dinitrophenylethylene*, golden-yellow needles, m. p. 81°, which on hydrolysis by alcoholic potassium hydroxide gives benzonitrile, potassium carbonate, and potassium nitrite. This decomposition is considered to be the outcome of a preliminary intramolecular change involving the migration of an oxygen atom:

$$C_2HPh(NO_2)_2 \longrightarrow NO\cdot CPh⁚C(OH)\cdot NO_2 \longrightarrow OH\cdot N⁚CPh\cdot CO\cdot NO_2 \xrightarrow[(KOH)]{} OH\cdot N⁚CPh\cdot CO_2H + KNO_2;\ OH\cdot N⁚CPh\cdot CO_2H \xrightarrow[(2KOH)]{} Ph\cdot CN + 2H_2O + K_2CO_3.$$

Both the dinitrostilbenes originally obtained by Schmidt (A., 1901, i, 226) by treating tolane with nitrogen peroxide yield the same tetraphenylpiperazine (Schmidt, *loc. cit.*) on reduction with gaseous hydrogen in the presence of palladium black. The oxime of deoxybenzoin is in each case obtained as a by-product.

[With H. WAGNER.]—Both the dinitrostilbenes, when digested with methyl alcoholic potassium hydroxide, are converted into the *acetal* of α-*nitrodeoxybenzoin*, which crystallises in long, white needles, m. p. 202—203°. α-*Nitro*-β-*methoxystilbene*, yellow prisms, m. p. 88—89°, can also be isolated and is evidently an intermediate product:

$$NO_2\cdot CPh⁚CPh\cdot NO_2 \longrightarrow NO_2\cdot CPh(OMe)\cdot CHPh\cdot NO_2 \longrightarrow OMe\cdot CPh⁚CPh\cdot NO_2 \longrightarrow CPh(OMe)_2\cdot CHPh\cdot NO_2.$$

C. K. I.

Isomerisation of 1-Phenylindene during Pyrogenic Distillation (A New Hydrocarbon). FRITZ MAYER and ADOLF SIEGLITZ [with WILLY LUDWIG] (*Ber.*, 1921, **54**, [*B*], 1397—1402).—Since the constitution of fluoranthene has recently been established with practical certainty (this vol., i, 248), the authors have resumed their efforts to synthetise the hydrocarbon, and for this reason have subjected 1-phenylindene to pyrogenic distillation. In the place of the expected fluoranthene, however, they have obtained a hydrocarbon, $C_{15}H_{12}$, which is isomeric with 1-phenylindene but completely different from it in its chemical behaviour. It is not identical with 2-phenylindene, and its constitution must be represented by one of the formulæ $C_6H_4<\begin{matrix}CH\\|\\CH\end{matrix}>CHPh$ and $\begin{matrix}C_6H_4\cdot CH\\|\quad\quad|\\CH_2-CH\end{matrix}>C_6H_4$.

1-Phenylindene has b. p. 153—154°/14 mm., m. p. 23°. It is reduced by sodium in boiling alcoholic solution to 1-*phenylhydrindene* b. p. 148—150°/13 mm. With benzaldehyde it gives 1-*phenyl-3-benzylideneindene*, yellow needles, m. p. 77·5°, and with terephthalaldehyde it yields 1 : 1′-*diphenyl*-3 : 3′-*terephthalylidenedi-indene*, $C_6H_4\left(CH{:}C{<}{}^{C_6H_4}_{-CH}{>}CPh\right)_2$, lustrous, red needles, m. p. 231—232°, whereas *p*-chlorobenzaldehyde and anisaldehyde give the corresponding *compounds*, golden-yellow needles, m. p. 95°, and lustrous, orange leaflets, m. p. 97°. Oxidation converts 1-phenylindene into *o*-benzoylbenzoic acid.

Pyrogenic distillation of 1-phenylindene gives the *hydrocarbon*, $C_{15}H_{12}$, colourless leaflets, m. p. 167·5°, which is not reduced by sodium and alcohol or by hydrogen and palladium, and yields feebly coloured compounds of high melting point when condensed with aldehydes. It does not combine with bromine. Oxidation with potassium permanganate transforms it into *benzil*-o-*carboxylic acid*, pale yellow needles, m. p. 141°.

2-*Phenylindene*, b. p. 167—170°/12 mm., is prepared by the reduction of 2-phenylindene-1-one by aluminium amalgam in moist ethereal solution and treatment of the product with boiling dilute sulphuric acid.

1-Phenyl-2-methylindene, pale yellow, lustrous leaflets, m. p. 57·5°, b. p. 177°/14 mm., is prepared by the action of magnesium phenyl bromide on 2-methylindene-1-one; it is unaffected by pyrogenic distillation.

1-Methylindene, b. p. 99—102°, is not affected by pyrogenic distillation; with terephthalaldehyde it gives 3 : 3′-*terephthalylidene*-1 : 1′-*dimethyldi-indene*, $C_6H_4\left(CH{:}C{<}{}^{C_6H_4}_{-CH}{>}CMe\right)_2$, orange crystals, m. p. 224°. H. W.

Di*cyclo*hexylamine and *cyclo*Hexylaniline. G. Fouque (*Ann. Chim.*, 1921, [ix], **15**, 291—332).—For the most part, a résumé of work already published (A., 1918, i, 106, 164). Certain new compounds are described. Di*cyclo*hexylamine gives a *hydrofluoride* and a *dihydrofluoride*, a *hydrobromide*, a *hydriodide*, a *nitrate*, a *hydrogen phosphate*, $(C_6H_{11})_2NH,H_3PO_4$, a *chromate*, a *dichromate*, a *tri-chromate*, an *acetate*, m. p. 65°, an *oxalate*, m. p. 206°, and a *picrate*, m. p. 173°. When its solution in carbon bisulphide is left to evaporate, it gives *di*cyclo*hexylamine di*cyclo*hexyldithiocarbamate*, $(C_6H_{11})_2N{\cdot}CS_2H,NH(C_6H_{11})_2$, m. p. 111°. With *iso*cyanic acid, it yields *di*cyclo*hexylcarbamide*, m. p. 247°. With alkyl iodides, di*cyclo*hexylamine reacts to give quaternary ammonium iodides of which *di*cyclo*hexyldimethylammonium iodide*, m. p. 216°, and *di*cyclo*hexyldiethylammonium iodide*, m. p. 224°, were prepared. Other compounds prepared from di*cyclo*hexylamine were *di*cyclo*hexylchloroamine*, $(C_6H_{11})_2NCl$, m. p. 26°; *di*cyclo*hexylnitrosoamine*, $NO{\cdot}N(C_6H_{11})_2$, m. p. 105°; *di*cyclo*hexylacetamide*, m. p. 102°, and *di*cyclo*hexylbenzamide*, m. p. 77°.

*cyclo*Hexylaniline gave a *hydrofluoride*, a *hydrobromide*, m. p. 184°,

a *hydriodide*, m. p. 176°, a *nitrate*, a *phosphate*, m. p. 175°; an *oxalate*, m. p. 186°, a *picrate*, m. p. 164°; *phenyl*cyclo*hexylcarbamide*, m. p. 221°; cyclo*hexylethylaniline*, b. p. 288°/764 mm.; 163°/30 mm.; d° 0·999; *phenyl*cyclo*hexylnitrosoamine*, m. p. 37°; cyclo*hexylacetanilide*, m. p. 66°; *phenyl*cyclo*hexylbenzamide*, m. p. 102°; b. p. 243°/20 mm. W. G.

The Solubility and Volatility of the Chloro- and Nitroanilines and of their Acetyl Derivatives. NEVIL VINCENT SIDGWICK and HOWARD ERNEST RUBIE (T., 1921, **119**, 1013—1024).

Some Derivatives of *p*-Hydroxyphenylglycine. L. GALATIS (*Helv. Chim. Acta*, 1921, **4**, 574—579).—p-*Hydroxyphenylaminoacetonitrile*, $HO\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN$, leaflets, m. p. 100°, which cannot be distilled without decomposition, is prepared by the successive addition of sodium hydrogen sulphite and formaldehyde to an aqueous solution of *p*-aminophenol hydrochloride and treatment of the product with potassium cyanide. It gives an *acetyl* derivative, colourless crystals, m. p. 75°, and, by the action of sodium chloroacetate, the *semi-nitrile* of p-*hydroxyphenylaminodiacetic acid.* In addition to *p*-hydroxyphenylglycine, p-*hydroxyphenylaminodiacetic acid*, $HO\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, is formed by the action of chloroacetic acid on *p*-aminophenol; it crystallises in small, colourless needles, decomp. about 160°; the *sodium* and p-*aminophenyl* salts and the *acetyl* derivative, colourless crystals, are described. The corresponding *hydrochloride* is very readily hydrolysed in aqueous solution. *p*-Hydroxyphenylglycine likewise forms a *hydrochloride*, long, prismatic crystals, which is decomposed with equal readiness by water. H. W.

Aromatic Nitro-derivatives. XIII. Substitution in the Benzene Nucleus. M. GIUA and A. ANGELETTI (*Gazzetta*, 1921, **51**, i, 318—324. Compare this vol., i, 198).—It has been already shown that the 3-nitro-group of 3 : 4 : 6-trinitrotoluene is readily eliminated by a moderately mild reaction when the alcoholic solution of the nitro-compound is treated with a base, such as ammonia, hydrazine, or phenylhydrazine. It is now found that similar displacement of the 3-nitro-group may be effected by *p*-aminoacetophenone, *p*-aminoazobenzene, or *p*-tolylhydrazine, additive compounds being formed as a preliminary to the substitution. The results obtained, together with those previously published, show that when, in a series of isomeric trinitrobenzene derivatives, the form symmetrical with respect to the nitro-groups produces an additive compound with a given primary base, the other isomerides also react with that base, giving, first, additive compounds and subsequently substitution derivatives.

2 : 4-*Dinitro-4′-acetyldiphenylamine*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4Ac$, prepared by the interaction of 4-chloro-1 : 3-dinitrobenzene (1 mol.) and *p*-aminoacetophenone (1 mol.) (compare Giua, Marcellino, and Curti, this vol., i, 193), separates in small, reddish-yellow prisms

or garnet-red crystals, m. p. 185°, gives a reddish-yellow coloration with concentrated sulphuric acid, forms soluble, reddish-brown salts with alcoholic alkali hydroxide, and yields a canary-yellow nitro-compound when heated with nitric acid (*d* 1·4).

The 2 : 4 : 5-*trinitrotoluene*—p-*aminoacetophenone* additive compound, $C_{15}H_{14}O_7N_4$, crystallises in orange-yellow prisms, m. p. 94—95°, and when crystallised from alcohol undergoes gradual transformation into 4-*acetylphenyl*-4′ : 6′-*dinitro*-m-*tolylamine*, $C_6H_2Me(NO_2)_2·NH·C_6H_4Ac$, which is better obtained by heating the reacting compounds in 95% alcoholic solution, and crystallises in lustrous, garnet-red prisms, m. p. 165—166°; it dissolves in sulphuric acid to a yellow solution, and gives an intense dark-red coloration with alkali in alcoholic solution. Its *phenylhydrazone*, $C_{21}H_{19}O_4N_5$, forms lustrous, brownish-red lamellæ, m. p. 189°, and gives a red coloration with concentrated sulphuric acid.

The 3 : 4 : 6-*trinitrotoluene*—p-*aminoazobenzene* additive compound, $C_{19}H_{16}O_4N_6$, crystallises in lustrous, purple plates, m. p. 155—156°, and is accompanied by p-*benzeneazophenyl*—4′ : 6′-m-*toluidine*, $N_2Ph·C_6H_4·NH·C_6H_2Me(NO_2)_2$, which forms reddish-yellow crystals, m. p. 186—187°.

4 : 6-*Dinitro*-m-p-*hydrazotoluene*, $C_6H_2Me(NO_2)_2·NH:NH·C_6H_4Me$, formed from 3 : 4 : 6-trinitrotoluene and *p*-tolylhydrazine, crystallises in reddish-yellow, lustrous lamellæ or large, reddish-brown plates, m. p. 159—160° (decomp.).

Investigation of the binary system 3 : 4 : 6-trinitrotoluene—*p*-aminoacetophenone by the freezing-point method indicates the existence of a molecular compound (1 mol. : 1 mol.), m. p. about 81°; the fused mixtures are intensely red. T. H. P.

Additive Compounds of Arylamines with Nitro-derivatives of Naphthalene. J. J. SUDBOROUGH, N. PICTON, and D. D. KARVÉ (*J. Ind. Inst. Sci.*, 1921, **4**, 43—58. Compare Sudborough, T., 1911, **99**, 209).—A record of experiments carried out to ascertain whether tri- and tetra-nitronaphthalenes form additive compounds similar to those of 1 : 3 : 5-trinitrobenzene. The following substances have been prepared :

Compounds of 1 : 3 : 5-trinitronaphthalene :—with α-naphthylamine, deep purple-black prisms, m. p. 135·5°; with β-naphthylamine, purplish-red flat needles, m. p. 145·5—146°; with benzidine, black prisms, m. p. 138°; with anisidine, black crystals, m. p. 128°; with ψ-cumidine, black needles, m. p. 101°; with *m*-phenylenediamine, deep chocolate needles, m. p. 170°; with 1 : 5-naphthylenediamine, thin, black needles, m. p. 243° (decomp.); with α-naphthylethylamine, reddish-black needles, m. p. 109°; with diphenylamine, dark red needles from mixture of alcohol and benzene, deep brown plates from toluene, m. p. 101°; with dimethylaniline, black prisms, m. p. 102°; with β-naphthyldiethylamine, long, black needles, m. p. 57—58°; with carbazole, red needles, m. p. 166°.

Compounds of 1 : 3 : 8-trinitronaphthalene :—with α-naphthylamine, $2C_{10}H_5(NO_2)_3,C_{10}H_7·NH_2$, deep crimson-red needles, m. p. 145—151°, and $C_{10}H_5(NO_2)_3,C_{10}H_7·NH_2$, dark brown prisms, m. p.

125—140°, also obtained from toluene as violet-black plates; with β-naphthylamine, deep red prisms, m. p. 132—133°.

1 : 4 : 5-Trinitronaphthalene with α-naphthylamine, dark red needles, m. p. 67—68°.

Compounds of 1 : 3 : 5 : 7-tetranitronaphthalene with α-naphthylamine, black needles, m. p. 220° (decomp.); with β-naphthylamine, black needles, m. p. 220—221°; with β-naphthyldiethylamine, dark green needles, m. p. 134—136°.

Compounds of 1 : 3 : 6 : 8-tetranitronaphthalene with naphthalene, lemon-yellow needles, m. p. 191—192°; with anthracene, deep red needles, m. p. 212—214°; with phenanthrene, orange needles, m. p. 243°; with acenaphthene, deep red prisms from benzene, orange needles from acetone, m. p. 125°; with aniline, dark brown solid, m. p. 154°; with α-naphthylamine, deep purple needles, m. p. 204—205°; with β-naphthylamine, deep brown plates, m. p. 211—212°; (the two last-named yield *acetyl* derivatives, m. p. 184—185° and 200—201° respectively); with benzidine, black needles, m. p. 194°; with ψ-cumidine, black needles, m. p. 155°; with dianisidine, black, crystalline powder, m. p. 205°; with α-naphthylmethylamine, purplish-black needles, m. p. 165°; with α-naphthylethylamine, black needles, m. p. 134°; with diphenylamine, black needles, m. p. 185°; with phenyl-β-naphthylamine, violet-brown needles, m. p. 173—174°; with benzyl-α-naphthylamine, black needles, m. p. 160°; with *p*-tolyl-β-naphthylamine, deep black needles, m. p. 150°; with dimethyl-aniline, black prisms, readily decomposed; with β-naphthyldiethylamine, black plates, m. p. 122—123°; with quinoline, dark brown solid, m. p. 123—124°; with *iso*quinoline, dark brown solid, m. p. 137°; with tetrahydroquinoline, m. p. 112°; with tetrahydro*iso*quinoline, m. p. 85—87°; with β-naphthyl ethyl ether, scarlet leaflets, m. p. 140—140·5°; with benzaldehydephenylhydrazone, violet-brown needles, m. p. 200°; with acetophenonephenylhydrazone, small, black, flat crystals, m. p. 171°; with phenyl cinnamylidenemethyl ketone, bright yellow needles, m. p. 192°; with distyryl ketone, lemon-yellow needles, m. p. 234°.

Compounds of 1 : 3 : 5 : 8-tetranitronaphthalene with α-naphthylamine, black needles, m. p. 162° (decomp.); with β-naphthylamine, bronze-green needles, m. p. 163—164° (*acetyl* derivative, scarlet needles, m. p. 158°); with dimethylaniline, black needles, m. p. 113°; with β-naphthyldiethylamine, black needles, m. p. 118—119°.

The conclusion is drawn that the number and position of the nitro-groups affect the capacity of the nitro-compound to yield stable additive compounds, this being most marked with the maximum number of nitro-groups in the meta-position with respect to each other. H. J. E.

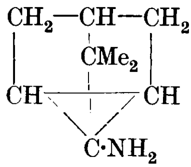
Preparation of Derivatives of Tetrahydro-β-naphthylamine. TETRALIN G. M. B. H., Berlin (D.R.-P. 335476; from *Chem. Zentr.*, 1921, ii, 1064).—*ac*-β-Bromo-α-hydroxytetrahydronaphthalene or analogous compounds (this vol., i, 407) are treated with ammonia or primary or secondary amines. The replacement of

the bromine atom takes place without formation of naphthalene. The hydroxy-amines are very active physiologically and find a use as drugs. By shaking β-bromo-α-hydroxytetrahydronaphthalene with concentrated aqueous ammonia and adding concentrated sodium hydroxide solution, β-*amino-α-hydroxytetrahydronaphthalene* separates in crystals, m. p. 112°; the *hydrochloride* has m. p. 227°. β-*Diethylamino-α-hydroxytetrahydronaphthalene* is prepared by heating the β-bromo-α-hydroxy-compound with diethylamine in a closed vessel on a water-bath; it is a thick, yellow liquid, b. p. 170°/10 mm. β-*Methylamino-α-hydroxytetrahydronaphthalene* prepared similarly, using methylamine, is a thick, colourless liquid, becoming brown on exposure to air, b. p. 168—169°/10 mm.; the *picrate* has m. p. 172° and the *hydrochloride* m. p. 184—185°. β-*Dimethylamino-α-hydroxytetrahydronaphthalene* is similarly prepared; it forms colourless crystals, m. p. 40°, b. p. 157—158°/10 mm.; the *picrate* has m. p. 140°; the *hydrochloride*, m. p. 174—175°; the *methiodide*, m. p. 140°. It gives with benzoyl chloride and alkali an oily *benzoyl* compound and with *p*-nitrobenzoyl chloride a yellow *nitrobenzoyl* derivative of the composition $CH_2<\begin{matrix}C_6H_4\cdot CH\cdot O\cdot CO\cdot C_6H_4\cdot NO_2\\ CH_2-CH\cdot NMe_2\end{matrix}$, m. p. 112°. From β-bromo-α-ethoxytetrahydronaphthalene and dimethylamine, β-*dimethylamino-α-hydroxytetrahydronaphthalene* is obtained as a colourless liquid, b. p. 152°/13 mm.; the *picrate* has m. p. 199°, the *methiodide*, m. p. 166°. β-*Piperidino-α-ethoxytetrahydronaphthalene*, similarly prepared, using piperidine, has b. p. 170/11 mm.; the *picrate* has m. p. 166°. β-*Dimethylamino-α-acetoxytetrahydronaphthalene*, $OAc\cdot C_{10}H_{10}\cdot NMe_2$, obtained by an analogous reaction, is a thick oil. By hydrolysis, the α-hydroxy-compound is formed. G. W. R.

***apo*Tricyclol, a Derivative of *cyclo*Propanol and its Ketonisation.** P. Lipp and C. Padberg (*Ber.*, 1921, **54**, [*B*], 1316—1329).—In continuation of previous work (A., 1920, i, 491), the authors have prepared *apo*tricyclol in the expectation that it, like the simpler *cyclo*propanol compounds, would show unusual reactions in consequence of the great strain in the three-membered ring. This is found to be the case; in the presence of dilute acids it undergoes isomerisation to camphenilone. It can, however, scarcely be classed as a typical enolic compound, since it does not give a coloration with ferric chloride or show the behaviour typical of a substance containing the hydroxyl group; the only strictly alcoholic derivative which could be prepared is the phenylurethane, other reagents leading to the formation of secondary products due to the instability of the trimethylene ring.

Tricyclenic acid is successively converted into the corresponding chloride and amide, and the latter is transformed by bromine and sodium methoxide in absolute methyl alcoholic solution into apo*tricyclylmethylurethane*, $C_9H_{13}\cdot NH\cdot CO_2Me$, prisms, m. p. 85·5—86° (corr.), small amounts of *tricycloyl*apo*tricyclylcarbamide*, $C_9H_{13}\cdot NH\cdot CO\cdot NH\cdot CO\cdot C_9H_{13}$, colourless needles, decomp. 238—239° (corr.), when slowly heated, being formed as by-product.

The urethane is converted by boiling sulphuric acid (40%) into camphenilone, b. p. 74—77°/15 mm. [identified as the semicarbazone, m. p. 223° (decomp.)], is almost unaffected by boiling aqueous or methyl-alcoholic potassium hydroxide solution, and is smoothly hydrolysed by molten potassium hydroxide at 160° to apo*tricyclylamine* (annexed formula), b. p. 176·8—177°/ atmospheric pressure, m. p. about 104°, which loses ammonia and becomes converted into a viscous, yellow oil when exposed to the air for a few days. Particularly if the temperature during hydrolysis is allowed to rise somewhat, the formation of camphenilone and camphenilol is also observed, the former arising from fission of the trimethylene ring by addition of water and elimination of ammonia, the latter being produced by reduction of the ketone by the liberated methyl alcohol: $C_9H_{13}\cdot NH\cdot CO_2Me \xrightarrow{H_2O} C_9H_{13}\cdot NH_2 + CO_2 + MeOH$. The following derivatives of *apo*tricyclylamine are described; *sulphate, hydrochloride, platinichloride*, orange-yellow prisms; *picrate*, yellow, prismatic crystals, m. p. about 200° (violent decomp.); *phenylcarbamide*, colourless needles, m. p. 222° (corr.); s-*diapo*tricyclyl*carbamide*, decomp. 243° when slowly heated; (?) apo*tricyclylcarbimide*, apo*tricyclylcarbamide*, small needles, m. p. 173—174° (corr.); *benzoyl*apo*tricyclylamine*, prisms, m. p. 173° (corr.); *acetyl*apo*tricyclylamine*, flat prisms, m. p. 177° (corr.), which sublime with unusual readiness.



*apo*Tricyclylamine hydrochloride is converted by sodium nitrite in cold solution into the corresponding *nitrite*, a sandy precipitate, which is converted in hot solution into apo*tricyclol*, long needles, m. p. 75—80°, b. p. 82—86°/12·5 mm.; this is converted into a viscous, yellow oil when exposed to the air for a few hours, but it can be preserved for a longer period in an atmosphere of hydrogen; the corresponding *phenylurethane* crystallises in long needles, m. p. 121·6—122° (corr.). Boiling dilute mineral acids transform the alcohol into camphenilone, which is also formed when it is heated in an atmosphere of dry hydrogen at 193°. Attempts to form *apo*tricyclol by the enolisation of camphenilone, for example, by the action of acetic anhydride and sodium acetate, were unsuccessful, the original material being recovered unchanged. Conversely, attempts to acetylate the alcohol either with acetic anhydride or acetyl chloride and pyridine gave chiefly camphenilone with only traces of an apparently acetylated product. Phosphorus pentachloride transforms *apo*tricyclol into camphenilone dichloride, m. p. 168—169°, the hydrogen chloride primarily formed being added to the initial product with rupture of the bond between the carbon atoms, 1 and 2. *apo*Tricyclol is not affected by an ethereal solution of diazomethane; attempts to effect the desired methylation in the presence of sodium showed that the metal dissolves in an ethereal solution of *apo*cyclol without evolution of hydrogen, forming the *sodium* derivative of camphenilonepinacone, $C_8H_{14}\cdot C(ONa)\cdot C(ONa)\cdot C_8H_{14}$, which is converted in part by methyl iodide but completely by methyl sulphate into the dimethyl ether

of camphenilonepinacone; *apo*cyclol methyl ether could not be characterised definitely owing to lack of material.

H. W.

Influence of Position on the Solubility and Volatility of the Mono- and Di-nitrophenols. NEVIL VINCENT SIDGWICK and WILFRID MAJOR ALDOUS (T., 1921, **119**, 1001—1012).

Metallic Derivatives of Nitrophenolic Compounds. I. Interaction of Barium, Strontium, and Calcium Hydroxides with the Mononitrophenols. ARCHIBALD EDWIN GODDARD (T., 1921, **119**, 1161—1165).

Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXVII. The Binary Systems of *m*- and *p*-Aminophenol and Phenols or Nitro-compounds. ROBERT KREMANN, EGBERT LUPFER, and OTHMAR ZAWODSKY (*Monatsh.*, 1921, **41**, 499—542. Compare A., 1920, i, 554).—The following binary systems have been investigated: *m*-aminophenol and phenol; *p*-toluidine and β-naphthol; aniline and β-naphthol; aniline and α-naphthol; *m*-aminophenol and β-naphthol; *m*-aminophenol and α-naphthol; *m*-aminophenol and catechol, *m*-aminophenol and resorcinol; *m*-aminophenol and quinol; *m*-aminophenol and pyrogallol; *m*-aminophenol and *o*-nitrophenol; *m*-aminophenol and *m*-nitrophenol; *m*-aminophenol and *p*-nitrophenol; *m*-aminophenol and *m*-dinitrobenzene; *m*-aminophenol and *o*-dinitrobenzene; *m*-aminophenol and 2 : 4-dinitrotoluene; *p*-aminophenol with phenol, α-naphthol, β-naphthol, and resorcinol.

m-Aminophenol gives an equimolecular compound with phenol which is remarkably little dissociated in the molten mass. *p*-Toluidine yields an equimolecular compound with β- or α-naphthol, whereas aniline gives a single compound with β-naphthol but two different compounds with α-naphthol. The introduction of the hydroxyl group in the meta position in aniline inhibits combination with α- but not with β-naphthol. Whereas aniline unites with quinol (2 : 1 molecular proportions), with catechol (1 : 1), and with pyrogallol (2 : 1), *m*-aminophenol combines with quinol, but not with catechol, resorcinol, or pyrogallol. *m*-Aminophenol resembles aniline in giving a simple eutectic with *o*- and *m*-nitrophenol and an equimolecular compound with *p*-nitrophenol. In contrast with aniline, *m*-aminophenol does not unite with *o*- or *m*-dinitrobenzene or with 2 : 4-dinitrotoluene.

Experiments with *p*-aminophenol could not be followed out systematically by reason of the instability of the substance at elevated temperatures. In the most favourable cases, the concentration of the aminophenol does not exceed 50% by weight, but it is nevertheless possible to show that the substance does not give solid compounds with phenol, α- or β-naphthol, or resorcinol, this result being probably due to the relatively slight solubility of *p*-aminophenol in the molten mixture.

The results are interpreted in terms of steric hindrance and total affinity.

H. W.

Acetic Acid Derivatives of *p*-Anisidine. J. HALBERKANN (*Ber.*, 1921, **54**, [*B*], 1152—1167).—p-*Anisylglycine*,

$$OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H,$$

irregular rectangular platelets, m. p. 154—157° (decomp.), according to the rate of heating, is conveniently prepared by warming a mixture of *p*-anisidine, sodium acetate, and a little water with chloroacetic acid; the colour reactions of the substance are fully described, as are also its *copper* salt, small, yellowish-green needles, and *zinc* salt, colourless, prismatic needles. Its *acetyl* derivative crystallises in coarse needles, m. p. 185°. *Ethyl* p-*anisylaminoacetate*, from *p*-anisidine and ethyl chloroacetate in ethyl acetate solution, forms plates or prisms, m. p. 57—58°, whereas the corresponding *acetyl* derivative is a colourless, stable liquid. p-*Anisylaminoacetamide*, plates or needles, m. p. 146—147°, is prepared by the action of alcoholic ammonia on the ester at 100°. *Chloroaceto*-p-*anisidide*, m. p. 121°, is prepared from *p*-anisidine and chloroacetyl chloride in cold benzene solution, and is converted by hot aqueous ammonia (*d* 0·910) into the tertiary *amine*,

$$(OMe\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2)_3N,$$

colourless, rectangular platelets, m. p. 205°, mixed with smaller amounts of the secondary *amine*, $(OMe\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2)_2NH$, colourless, irregular leaflets, m. p. 141°. p-*Anisylaminoaceto*-p-*anisidide*, rectangular leaflets, m. p. 134°, is obtained from *p*-anisidine and *p*-anisidinoacetic acid at 135° or from chloroaceto-*p*-anisidide and *p*-anisidine at 120—140°; the corresponding *acetyl* derivative crystallises in colourless, slender needles, m. p. 138°. *Di*-p-*anisidinoaceto*-p-*anisidide*, $(OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO)_2N\cdot C_6H_4\cdot OMe$, forms lustrous, rhombic leaflets, m. p. 185°.

Chloroaceto-*p*-anisidide is transformed by the action of an excess of sodium ethoxide in cold alcoholic suspension into the piperazine *derivative*, $OMe\cdot C_6H_4\cdot N{<}{\substack{CH_2\cdot CO\\ CO\cdot CH_2}}{>}N\cdot C_6H_4\cdot OMe$, lustrous, rhombic leaflets, m. p. 256°, which is more advantageously prepared by heating anisidinoacetic acid at 150—160° in an atmosphere of nitrogen; it is converted by boiling alcoholic potassium hydroxide solution into the *acid*,

$$OMe\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe,$$

hexagonal prisms, m. p. 128°, with loss of water after softening at about 110° and has m. p. 256° after resolidification. p-*Anisidinoacetomethyl*-p-*anisidide*, $OMe\cdot C_6H_4\cdot NMe\cdot CO\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, is obtained in small amount as by-product in the preparation of the piperazine by heating anisidinoacetic acid or from *p*-anisidinoacetic acid and methyl-*p*-anisidine at 145—150°; it forms colourless, rectangular prisms, m. p. 119—120°, and is most conveniently obtained by cautiously heating *p*-anisidine with *chloroacetomethyl*-p-*anisidide*, colourless plates, m. p. 57°.

p-*Anisidinediacetic acid*, $OMe\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, colourless rods, m. p. 122—123° (decomp.), is obtained as by-product in the preparation of the corresponding mono-compound. It is transformed by being heated with *p*-anisidine into the corresponding *di*-p-*anisidide*, colourless, matted needles, m. p. 184—185°, and *methyl*-

p-*anisidinoaceto*-p-*anisidide*, $OMe\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, long needles, m. p. 129—130°.

The action of heat on a mixture of anisidinoacetic acid (2 mols.) and chloroaceto-*p*-anisidide (1 mol.) leads to the formation of the *compound*, $OMe\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4\cdot OMe$, colourless plates, m. p. 147° (decomp.) after softening at 140°, which is transformed by boiling acetic anhydride into the *substance*,

$$OMe\cdot C_6H_4\cdot N{<}{\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}}{>}N\cdot C_6H_4\cdot OMe,$$

colourless platelets, or long needles, m. p. 152°. H. W.

The Tetrahydronaphthols. A. Brochet and R. Cornubert (*Compt. rend.*, 1921, **172**, 1499—1500. Compare *Bull. Soc. chim.*, 1913, [iv], **13**, 198).—The hydrogenation of α-naphthol under a pressure of fifteen atmospheres in the presence of reduced nickel yields 15% of *ar*-tetrahydro-α-naphthol, m. p. 68°, and 85% of ac-*tetrahydro-α-naphthol*, b. p. 139—140°/17 mm. (corr.); d_4^{17} 1·0896; n_D^{17} 1·5671, giving a *phenylurethane*, m. p. 121°. Under similar conditions, β-naphthol gives 25% of *ar*-tetrahydro-β-naphthol, m. p. 57·5°, and 75% of *ac*-tetrahydro-β-naphthol, b. p. 144·5—146·5°/20 mm. (corr.); d_4^{17} 1·0715; n_D^{17} 1·5523, giving a *phenylurethane*, m. p. 99°. W. G.

Condensations between Carbonyl Compounds and Resorcinol (or Orcinol) or Phloroglucinol. Astrid Cleve von Euler (*Arkiv Kem. Min. Geol.*, 1921, **8**, No. 3, 1—40).—The author gives a critical résumé of the literature dealing with the condensation of resorcinol or phloroglucinol with sugars and with aldehydes and ketones in general in presence of a condensing agent such as hydrochloric or sulphuric acid.

As regards the general course of the condensation of carbonyl compounds with resorcinol, the following conclusions are drawn: (1) One linking of the carbonylic oxygen is ruptured and the free valency thus arising attracts a hydrogen atom occupying at one and the same time an ortho- and a para-position to a hydroxyl group of the resorcinol molecule, the resorcinol residue passing to the vacant carbon linking; it may be, however, that all the ketonic carbonyls are first enolised. The hydroxyl formed from carbonyl in one of these ways is eliminated with an ortho-para-hydrogen atom of a resorcinol molecule (pure aldehydes, enolised ketones) or with a neighbouring methylic hydrogen (ketones); thus, from aldehydes there arise diresorcinol, and from ketones, monoresorcinol derivatives. With diresorcinol derivatives, anhydride-formation between the hydroxyls of each of the resorcyl components gives rise to three double-ring systems, which form the nuclei in leuco-bases of the xanthen group; the yellow or red colorations obtained are formed by the oxidation of these leuco-bases to hydroxyfluorones. Coloured benzopyranols may arise from anhydride-formation between a resorcinol residue and a suitably situated hydroxyl group in a hydroxy-ketone residue (ketose, acetylacetone), and since subsequent oxidation is unnecessary for the formation of chromophores, such hydroxycarbonyl compounds give intense colour

reactions instantaneously. This scheme may be developed to include the case in which a *m*-aminophenol forms a side-component to the resorcinol, the leuco-compound then being a hydroxyacridine and the coloured product an oxyacridine.

The results obtained by different authors who have investigated the condensation of various carbonylic compounds with phloroglucinol and *m*-polyphenols in general may be brought under a common heading if it is assumed that the initial phase of the reaction consists of an aldol condensation. Various cases are considered in detail, the manner in which condensation compounds may be formed between the carbonylic and hydroxylic compounds in different proportions with loss of varying proportions of water being discussed. T. H. P.

Nitration of Methylenedi-*p*-phenetidine. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1921, **4**, 580—588. Compare A., 1913, i, 850).—The preparation of nitro-derivatives of methylenedi-*p*-phenetidine (Bischoff and Schatz, A., 1899, i, 278) is rendered exceptionally difficult by the fact that the base suffers almost immediate fission into *p*-phenetidine in the presence of concentrated mineral acids or of acetic acid. The author has therefore examined the action on it of nitric acid (45%) at a temperature not exceeding 20°, and has isolated the nitrate, $C_{18}H_{24}O_2N_2,HNO_3$ or $C_{18}H_{22}O_2N_2,HNO_3$, colourless, prismatic needles, m. p. 159°, from which the *base*, $C_{18}H_{24}O_2N_2$ or $C_{18}H_{22}O_2N_2$, colourless prisms, m. p. 132°, is obtained; the *nitroso*-derivative, m. p. 217°, and *acetyl* compound, colourless, prismatic needles, m. p. 237°, of the latter are described.

The action of formaldehyde on *p*-phenetidine in the presence of hydrochloric acid has been re-examined and found to be more complicated than supposed by Goldschmidt (A., 1898, i, 184) and by Lepetit and Maimeri (A., 1917, i, 452). In addition to Goldschmidt's compound, m. p. 139°, two further *bases*, m. p. 200° and 107° respectively, have been isolated, but the analytical data are not sufficient to permit conclusions to be drawn as to their composition. In the presence of nitric acid (45%), formaldehyde and *p*-phenetidine give the nitrate (m. p. 159°) of the base, m. p. 132°, described above, but in more dilute solution the bases, m. p. 140° and 200° respectively, are obtained. H. W.

β-Hydroxy-β-3 : 4-methylenedioxyphenylethylamine and its Derivatives. FREDERICK ALFRED MASON (T., 1921, **119**, 1077—1081).

Action of the Grignard Reagent on certain Organo-sulphur Compounds. HARRY HEPWORTH and HENRY WILLIAM CLAPHAM (T., 1921, **119**, 1188—1198).

The dehydration of α-Phenyl-ββ-dimethylbutane-α-ol and of αγ-Diphenyl-ββ-dimethylpropane-α-ol. (MLLE) JEANNE APOLIT (*Compt. rend.*, 1921, **172**, 1493—1496).—When α-phenyl-ββ-dimethylbutane-α-ol is dehydrated by passing its vapour over

infusorial earth at 300° the product is a mixture of γ-phenyl-β-methyl-Δ^{β}-pentene and β-phenyl-γ-methyl-Δ^{β}-pentene, which could not be completely separated by distillation. When αγ-diphenyl-ββ-dimethylpropane-α-ol is similarly dehydrated at 240°, it yields a mixture of αγ-diphenyl-β-methyl-Δ^{β}-butene and αβ-diphenyl-γ-methyl-Δ^{β}-butene. W. G.

Abnormal Iodine Values with Special Reference to the Sterols and Resins. IDA SMEDLEY MACLEAN and ETHEL MARY THOMAS (*Biochem. J.*, 1921, **15**, 319—333).—The Hübl method gives much higher values than that of Wijs in the case of phenol and α-naphthol, possibly because the latter is an enolising agent and retards a change to keto*cyclo*hexadiene, which in these cases may be a necessary preliminary to the addition of halogen (compare Ingle, A., 1904, ii, 456). With aliphatic carbonyl compounds, phenanthrene hydrocarbons, sterols, and resins (abietic acid), the Wijs numbers are higher than the Hübl values, and it is suggested that the acid of the Wijs reagent enolises the carbonyl compounds before addition of halogen takes place (compare Lapworth, T., 1904, **85**, 30). For abietic acid (with two double bonds), the Hübl value shows the addition of four and the Wijs value the addition of six atoms of iodine. Similarly with sterols, the Hübl value approximately indicates the number of double bonds present, whilst the Wijs value is much higher on account of substitution. Hence in a fat containing appreciable quantities of sterols, the Hübl method gives more accurately the degree of unsaturation than that of Wijs. G. B.

The Hydrobenzoin, Semihydrobenzoin, and Semipinacolic Transpositions. The Dehydration of Alkylhydrobenzoins. M. TIFFENEAU and A. ORÉKHOFF (*Bull. Soc. chim.*, 1921, [iv], **29**, 422—429).—A more detailed account of work already published (A., 1920, i, 672). W. G.

The Hydrobenzoin and Semipinacolic Transpositions of Propylhydrobenzoin and Butylhydrobenzoin. FRÉDÉRIC BILLARD (*Bull. Soc. chim.*, 1921, [iv], **29**, 429—445. Compare preceding abstract).—αβ-*Diphenylpentane*-αβ-*diol*, m. p. 119°, when dehydrated with cold concentrated sulphuric acid, gives propyldeoxybenzoin and αα-diphenylpentane-β-one. Propyldeoxybenzoin gives a *semicarbazone*, m. p. 125°, and reacts with magnesium phenyl bromide to give ααβ-*triphenylpentane*-α-*ol*, m. p. 106°. Diphenylacetaldehyde condenses with magnesium propyl iodide, giving αα-*diphenylpentane*-β-*ol*, b. p. 188—190°/13 mm.; d^{0} 1·05, which on oxidation yields αα-*diphenylpentane*-β-*one*, b. p. 185—186°/13 mm., giving a *semicarbazone*, m. p. 191—192°. With hot dilute sulphuric acid or oxalic acid melted in its own water of crystallisation, αβ-diphenylpentane-αβ-diol yields for the most part αα-*diphenylvaleraldehyde*, $CPh_2Pr\cdot CHO$, b. p. 189—191°/15 mm., giving an *oxime*, m. p. 117°, and a *semicarbazone*, m. p. 139°.

αβ-*Diphenylhexane*-αβ-*diol*, m. p. 125°, obtained by the action of benzoin on magnesium butyl iodide when dehydrated with cold,

concentrated sulphuric acid gives *butyldeoxybenzoin*, m. p. 64°, and *αα-diphenylhexane-β-one*, m. p. 38°. Butyldeoxybenzoin, obtained by the action of butyl bromide on sodium deoxybenzoin, gives with magnesium phenylbromide *ααβ-triphenylhexane-α-ol*, m. p. 115°. Diphenylacetaldehyde condenses with magnesium butyl iodide, giving *αα-diphenylhexane-β-ol*, m. p. 60—61°, which on oxidation yields *αα-diphenylhexane-β-one*, m. p. 38°, giving an *oxime*, m. p. 159°. When dehydrated with hot dilute sulphuric acid or molten oxalic acid, αβ-diphenylhexane-αβ-diol gives *αα-diphenylhexaldehyde*, $C_4H_9 \cdot CPh_2 \cdot CHO$, b. p. 194—196°/13 mm., and forms an *oxime*, m. p. 110°, and a *semicarbazone*, m. p. 153°. W. G.

Hydrobenzoin and Semipinacolic Transpositions in the Triarylethanediols with *p*-Methoxyl Substitution (Anisylglycols). A. ORÉKHOFF and M. TIFFENEAU (*Bull. Soc. chim.*, 1921, [iv], **29**, 445—459).—A more detailed account of work already published (A., 1920, i, 673). The following new compounds are described.

*αβ-Diphenyl-α-*p*-anisylethane-αβ-diol*, m. p. 197—198°. *Anisyldeoxybenzoin*, m. p. 88—89°, giving an *oxime*, m. p. 139—140°. *β-Phenyl-αα-di-*p*-anisylethane-αβ-diol*, m. p. 197—198°. *Phenyl di-*p*-anisylmethyl ketone*, m. p. 57—58°, giving an *oxime*, m. p. 164—165°. *αα-Diphenyl-β-anisylethane-αβ-diol*, m. p. 192—194°. *Diphenyl-*p*-anisylacetaldehyde*, $OMe \cdot C_6H_4 \cdot CPh_2 \cdot CHO$, m. p. 75—76°, giving a *semicarbazone*, m. p. 198—199°. *ααβ-Tri-*p*-anisylethane-αβ-diol*, m. p. 176—177°. *Tri-*p*-anisylacetaldehyde*, m. p. 125—126°, giving an *oxime*, m. p. 166—167°, and a *semicarbazone*, m. p. 175—176°. W. G.

Hypnotics. II. Derivatives of *cyclo*Hexanecarboxylic Acid. M. E. FOURNEAU, (MLLE) MONTAGNE, and JOSÉ PUYAL (*Anal. Fís. Quím.*, 1921, **19**, 192—198).—Derivatives of α-ethylvaleric acid show sedative properties. *cyclo*Hexanecarboxylic acid, which may be considered as related to α-ethylvaleric acid, and its derivatives might be expected to show similar properties. In a study of this acid and its derivatives, improved methods have been devised for the preparation of *cyclo*hexyl chloride, *cyclo*hexanecarboxylic acid, *cyclo*hexanecarboxyl chloride, bromo*cyclo*hexanecarboxylic acid, ethyl bromo*cyclo*hexanecarboxylate, hydroxy*cyclo*hexanecarboxylic acid, and ethyl hydroxy*cyclo*hexanecarboxylate. In addition, *bromo*cyclo*hexanecarboxyl chloride*, b. p. 115—118°/12 mm., was obtained by the action of bromine on *cyclo*hexanecarboxyl chloride. *Bromo*cyclo*hexanecarboxyl bromide*, formed by the action of excess of bromine on *cyclo*hexanecarboxylic acid in the presence of red phosphorus, has b. p. 113—115°/13 mm. *Bromo*cyclo*hexanecarboxylcarbamide* is formed by the action of carbamide on bromo*cyclo*hexanecarboxyl chloride or bromide; the product, m. p. 159—160°, is only slightly soluble in the ordinary solvents. *Bromo*cyclo*hexanecarboxylamide*, prepared by the action of ammonia on bromo*cyclo*hexanecarboxyl chloride or bromide, has m. p. 136°.

G. W. R.

The Influence of Position on the Solubilities of the Substituted Benzoic Acids. NEVIL VINCENT SIDGWICK and ELINOR KATHARINE EWBANK (T., 1921, **119**, 979—1001).

Interaction of Sulphur Monochloride and Organic Acid Amides. KUVERJI GOSAI NAIK (T., 1921, **119**, 1166—1170).

Preparation of *ar*-α-Tetrahydronaphtholcarboxylic Acid. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 335602; from *Chem. Zentr.*, 1921, ii, 1065).—When dry carbon dioxide is passed over the dry sodium salt of *ar*-α-tetrahydronaphthol for about one hour at 110° and the temperature raised to 210°, *ar-α-tetrahydronaphtholcarboxylic acid* is obtained as a white, crystalline powder, crystallising in needles from glacial acetic acid, m. p. 161—162°. The *acetyl* compound crystallises from 50% acetic acid in needles, m. p. 159°. The *acid sodium* salt forms nacreous crystals. With diazotised nitroanilines and their derivatives, for example, nitroaminophenolsulphonic acid, valuable azo-dyes are obtained. G. W. R.

The Reduction of Ethyl Naphthoate and a Case of Reduction of an Alcohol to a Hydrocarbon by Sodium and Absolute Alcohol. HERVÉ DE POMMEREAU (*Compt. rend.*, 1921, **172**, 1503—1504).—Ethyl α-naphthoate is reduced by sodium in absolute alcohol, giving *α-methyl-*(?)*-1 : 4-dihydronaphthalene*, b. p. 228°/760 mm., which yields a *dibromide*, m. p. 84°. This dihydronaphthalene is also obtained by the reduction of α-methylnaphthalene or α-naphthyl alcohol by the same reducing agent. W. G.

The Catalysts in the Reaction between Carbon Monoxide, Hydrogen Chloride, and Aromatic Hydrocarbons. A. KORCZYŃSKI and W. MROZIŃSKI (*Bull. Soc. chim.*, 1921, [iv], **29**, 459—462).—In the action of carbon monoxide and hydrogen chloride on aromatic hydrocarbons in the presence of aluminium chloride and cuprous chloride, the cuprous chloride as a catalyst may be replaced by nickelous, cobaltous, or ferric chloride or by tungsten chloride. Nickelous chloride gave the best yields, but in no case were they much above 50% of that obtained with cuprous chloride. W. G.

6-Aminopiperonaldehyde and its Derivatives. AUGUSTE RILLIET and LOUIS KREITMANN (*Helv. Chim. Acta*, 1921, **4**, 588—599).—The reduction of *o*-nitroaldehydes to the corresponding aminoaldehydes is generally complicated by the simultaneous formation of condensation products of the latter. It is, however, shown that 6-aminopiperonaldehyde and its derivatives can be readily prepared if the aldehydic group is protected by condensation with benzaldehyde or other aldehyde and reduction is effected by sodium sulphide: $4R\cdot NO_2+6Na_2S+7H_2O=4R\cdot NH_2+3Na_2S_2O_3+6NaOH$. The product of the reaction is subsequently hydrolysed by boiling water.

6-*Nitropiperonylidene*-p-*toluidine*, $CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CH{:}N\cdot C_6H_4Me$, long, pale yellow crystals, m. p. 121·5°, is prepared by heating 6-nitropiperonaldehyde with an equimolecular weight of *p*-toluidine at

120—130°, whereas the corresponding *compounds* from *o*-toluidine and *p*-anisidine form yellow needles, m. p. 128°, and yellow leaflets, m. p. 125·5°, respectively. On reduction, the substances give 6-*aminopiperonylidene*-p-*toluidine*, sulphur-yellow needles, m. p. 134·5°, 6-*aminopiperonylidene*-o-*toluidine*, yellow leaflets, m. p. 116°, and 6-*aminopiperonylidene*-p-*anisidine*, pale yellow leaflets or needles, m. p. 162°, respectively. Hydrolysis of these compounds in boiling, very slightly alkaline aqueous solution leads to the production of 6-*aminopiperonaldehyde*, the best yield (71%) being obtained with the *p*-toluidine compound; the aldehyde crystallises in large, pale yellow prisms, m. p. 107°, and is immediately decomposed by dilute acids with production of a red, amorphous mass. The *hydrochloride*, small, colourless needles which decompose on contact with air and the *mercurichloride*, m. p. 133°, are described. The *acetyl* derivative, colourless needles, m. p. 161° (*phenylhydrazone*, m. p. 205°), *benzoyl* derivative, long, pale yellow needles, m. p. 187·5°, *phenylhydrazone*, colourless leaflets, m. p. 222°, and oxime, m. p. 184°, were also prepared.

Diazotisation of 6-aminopiperonaldehyde is rendered somewhat difficult by reason of the susceptibility of the aldehyde to acids, and is best effected by dissolving the aldehyde in dilute acetic acid and cautiously adding the quantity of dilute mineral acid necessary for diazotisation. The following compounds are thus obtained: 6-bromopiperonaldehyde; 6-*chloropiperonaldehyde*, colourless needles, m. p. 113°; 6-*iodopiperonaldehyde*, colourless needles, m. p. 111°. Replacement of the amino- by the cyano-group could not be effected by diazotisation, and the replacement of the aldehyde by its oxime leads to the formation of the *azide*, $CH_2O_2{:}C_6H_2N_3{\cdot}CHO$, m. p. 122° (*phenylhydrazone*, m. p. 136°, p-*nitrophenylhydrazone*, m. p. 168°).

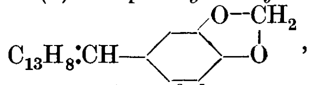
The condensation of 6-aminopiperonaldehyde with acetone in aqueous alkaline solution leads to the almost quantitative production of 6 : 7-methylenedioxyquinaldine, m. p. 150° (*hydrochloride*, colourless needles; *mercurichloride*, long, colourless needles, m. p. 208°; *picrate*, small, yellow needles, m. p. 182°; *platinichloride*, m. p. 261; methiodide, m. p. 273°). With methyl ethyl ketone, a similar product, long, colourless needles, m. p. 145°, b. p. 328—329°, is obtained which is regarded as 6 : 7-*methylenedioxy*-2 : 3-*dimethylquinoline* (*hydrochloride*, colourless needles which decompose before melting; *mercurichloride*, m. p. 282—284°; *picrate*, yellow leaflets, m. p. 230°; *platinichloride*, long, orange needles, m. p. 273°; *methiodide*, pale yellow needles, m. p. 249—250°). Acetophenone gives 6 : 7-methylenedioxy-2-phenylquinoline, m. p. 109° [*hydrochloride*, orange leaflets, m. p. 272°; *mercurichloride*, colourless needles, m. p. 258—259°; picrate, m. p. 195°; *platinichloride*, colourless leaflets; *methiodide*, yellow leaflets, m. p. 213° (decomp.)].

H. W.

New Reaction of Aldehydes. II. REMO DE FAZI (*Gazzetta*, 1921, **51**, i, 328—338. Compare A., 1916, ii, 457).—In consequence of the publication of Sieglitz's work on the fluorene series (A., 1920,

i, 27, 605), the author gives the results he has at present obtained (compare Thiele and Henle, A., 1906, i, 571).

With piperonaldehyde in presence of sodium ethoxide, fluorene gives two compounds: (1) 9-*Piperonylidenefluorene*,



which forms stellate aggregates of large, canary-yellow prisms, m. p. 71—72°, gives with concentrated sulphuric acid an intense emerald-green coloration gradually changing to violet-blue, and forms a *picrate*, $C_{21}H_{14}O_2,C_6H_3O_7N_3$, m. p. 195—198° (decomp.); when reduced in ethereal solution by means of aluminium amalgam, it is converted into 9-*piperonylfluorene*, $C_{13}H_9\cdot CH_2\cdot C_6H_3{:}O_2{:}CH_2$, which crystallises in slender, lustrous, white needles, m. p. 99—100°, and gives a scarcely perceptible yellow coloration with concentrated sulphuric acid. (2) A small proportion of an isomeric *compound*, $C_{21}H_{14}O_2$, which forms lustrous, orange-red needles, m. p. 183—184°, and gives a blue ring changing to violet when concentrated sulphuric acid is carefully added to its ethereal solution.

9-m-*Methylbenzylidenefluorene*, $C_{13}H_8{:}CH\cdot C_6H_4Me$, obtained from fluorene and *m*-tolualdehyde, forms an orange-yellow resin of pleasing odour, and gives a yellow and then a greenish-blue solution in concentrated sulphuric acid, whilst in alcoholic solution it gives a yellow coloration. Its *picrate*, $C_{21}H_{16},C_6H_3O_7N_3$, forms lustrous, orange-yellow needles, m. p. 104—105°. In chloroform solution, it combines with bromine, giving *dibromo*-9-m-*methylbenzylfluorene*, $C_{13}H_8Br\cdot CHBr\cdot C_6H_4Me$, as a pale yellow resin.

9-m-*Methylbenzylfluorene*, $C_{13}H_9\cdot CH_2\cdot C_6H_4Me$, obtained by reducing either the preceding dibromo-compound by means of zinc and acetic acid or 9-*m*-methylbenzylidenefluorene by means of aluminium amalgam, crystallises in slender, white needles, m. p. 111—112°, and gives no coloration with concentrated sulphuric acid.

9-*Cuminylidenefluorene*, $C_{13}H_8{:}CH\cdot C_6H_4Pr^{\beta}$, forms an orange-yellow resin of pleasing odour, and with concentrated sulphuric acid gives a greenish-yellow, and later a green, coloration, whilst in alcoholic solution it gives a yellow ring turning emerald-green.

9-p-*Dimethylaminobenzylidenefluorene*, $C_{13}H_8{:}CH\cdot C_6H_4\cdot NMe_2$, formed from fluorene and *p*-dimethylaminobenzaldehyde in presence of sodium ethoxide, crystallises in lustrous, orange-red needles, m. p. 135—136°, and with concentrated sulphuric acid gives a greenish-yellow coloration, which is obtained also in alcoholic solution. It is accompanied by a small proportion of another *compound*, which crystallises in garnet-red needles, m. p. 158—160°, but was not analysed.

9-p-*Dimethylaminobenzylfluorene*, $C_{13}H_9\cdot CH_2\cdot C_6H_4\cdot NMe_2$, obtained by reducing the preceding compound with aluminium amalgam, forms lustrous, golden-yellow needles, m. p. 119—120°, and gives no coloration with concentrated sulphuric acid, even in alcoholic solution.

The results obtained confirm the colour reaction which cyclic aldehydes give with fluorene or acenaphthene in presence of

concentrated sulphuric acid, but show clearly that such reaction is not due to the formation of condensation products. T. H. P.

Certain Nitronic Derivatives. L. Alessandri (*Gazzetta*, 1921, **51**, i, 75—89).—In consequence of the publication of papers by Semper and Lichtenstadt (A., 1918, i, 437) and by Staudinger and Miescher (A., 1919, i, 584) in which various nitronic derivatives already obtained by Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) and by Alessandri (A., 1915, i, 412, 888) are dealt with, the author gives further results he has obtained in this region. These indicate that the property of reacting with magnesium alkyl haloids is general with nitrones of the type CHR:NR:O. It remains to be seen if nitrones of the form CR_2:NR:O are, in general, devoid of this property; the N-phenyl ether of benzophenone-oxime remains unchanged when treated with the Grignard reagent (A., 1911, i, 544).

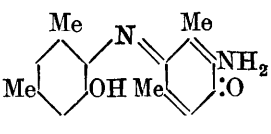
Reduction of the N-phenyl ether of benzophenoneoxime by means of zinc dust and ammonium chloride results in the formation of phenyliminobenzophenone; part of the latter undergoes further reduction to phenylbenzhydrylamine, the two reduction products then uniting to form an additive *compound*, CPh_2:NPh,$CHPh_2$·NHPh, which crystallises in lustrous, rhombohedral prisms, m. p. 83°, may readily be obtained from an alcoholic solution of its components, and is different in type from those previously described, as it contains only tervalent nitrogen and is free from the characteristic oxygen of the nitrones.

It has been already shown (A., 1915, i, 412) that the product obtained by oxidising benzylbenzhydrylhydroxylamine is the N-benzhydryl ether of benzaldoxime; the latter is now found to be accompanied by the isomeric N-benzyl ether of benzophenone-oxime, CPh_2:NO·CH_2Ph. The action of magnesium ethyl iodide on the benzhydryl ether of benzaldoxime gives a deep orange-yellow oil. The action of magnesium phenyl bromide on the same compound yields also a viscous, orange oil, and in addition a crystalline compound, which proves to be, not the dibenzhydryl-hydroxylamine, OH·N$(CHPh_2)_2$, expected, but its oxidation *product* of the structure CPh_2:NO·$CHPh_2$; the latter forms lustrous, prismatic needles, m. p. 167°, and is readily converted into dibenzhydrylamine (Friedel and Balsohn, A., 1881, 279) when reduced by means of aluminium amalgam. Dibenzhydrylamine forms long, slender, colourless needles, m. p. 139°, and its picrate, golden-yellow prisms, m. p. 202° (decomp.). T. H. P.

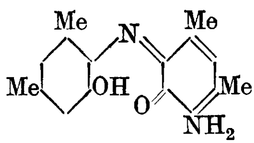
The Structural Isomerism of the Oximes. I. Criticism of the Hantzsch-Werner Hypothesis and a New Theory of the Constitution of Isomeric Oximes. Frederick William Atack (T., 1921, **119**, 1175—1184).

The Structural Isomerism of the Oximes. II. A Fourth Benzildioxime. Frederick William Atack and Leonard Whinyates (T., 1921, **119**, 1184—1188).

The Oxidation of Meta-substituted o-Aminophenols. K. VON AUWERS, E. BORSCHE, and R. WELLER (*Ber.*, 1921, **54**, [*B*], 1291—1316).—The investigation of the product obtained by the oxidation of *o*-amino-*m*-5-xylenol by air (Auwers and Borsche, A., 1916, i, 34) has been continued. It is shown to have the composition $C_{16}H_{18}O_2N_2$, and to contain a hydroxyl, a ketonic, and an amino-group. When hydrolysed with acetic and hydrochloric acids it regenerates *o*-amino-*m*-5-xylenol, but the fate of the remainder of the molecule could not be elucidated. These observations serve to eliminate all the possible formulæ except those annexed (I and II). The decision in favour of I is reached



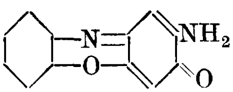
(I.)



(II.)

in the following manner. A bromine atom is introduced into the original phenol in the para-position to the hydroxyl group and the new substance is subjected to oxidation; the product closely resembles that derived from the simpler amine, but contains only one atom of bromine, the other being eliminated during the process of oxidation, thus necessarily yielding a *p*-quinone.

The investigation has a more general interest in throwing light on the constitution of the products of the oxidation of the simplest aminophenols and confirming Fischer and Jonas's formula (annexed)

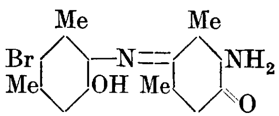


for the substance derived from *o*-aminophenol. In the case of the xylenol, the final formation of a tricyclic structure appears to be inhibited by the presence of the methyl group in the meta-position. As far as the present observations extend, this action appears to be general, since similar behaviour is encountered with 3-bromo-*o*-amino-*m*-cresol and with *o*-amino-*m*-cresol (compare Kehrmann, A., 1906, i, 210).

4-Amino-*m*-2:5-xyloquinone-5′-hydroxy-*m*-4′-xylylimide (formula I), lustrous, orange-yellow crystals, m. p. 185°, is most conveniently prepared by the oxidation of a solution of the aminoxylenol in sodium hydroxide by gaseous oxygen; the reaction proceeds more rapidly when hydrogen peroxide or potassium ferricyanide is employed, but the yields are not so good. The corresponding *hydrochloride*, $C_{16}H_{18}O_2N_2$,HCl, forms small, tile-red needles or an ochre-coloured powder. The *platinichloride* was analysed. The substance gives an *oxime*, pale, brownish-yellow leaflets, m. p. 199—200°, a *phenylhydrazone*, small, orange-red needles, m. p. 294—296°, and a *semicarbazone*, slender, yellow needles, m. p. 206—207° (*hydrochloride*, m. p. 267°); the properties of the latter substance in particular point to the possibility that these products are not true ketonic derivatives but the isomeric hydroxyazo-compounds. Mild treatment of the substance, m. p. 185°, with acetic anhydride alone or in the presence of pyridine leads to the isolation of the N-*acetyl* derivative, lustrous, orange-yellow leaflets, m. p. 219°, whilst more drastic and protracted action gives the

ON-*diacetyl* compound, sulphur-yellow needles, m. p. 149°. The N-*propionyl* and N-*acetyl*-O-*propionyl* derivatives crystallise in pale yellow needles, m. p. 182—183°, and yellow needles, m. p. 139—140° respectively, but attempts to prove that the di-derivatives are in reality ON- and not di-N-compounds by isolating the N-propionyl-O-acetyl compound were unsuccessful, since the N-propionate was converted by acetic anhydride into the diacetate. The quinoneimide is converted by diazotisation into the (?) *diazonium* base, reddish-yellow needles, which explodes at 175°; the diazo-solution is very slowly transformed when heated into the corresponding *phenol*, $C_{16}H_{17}O_3N$, m. p. 140—160°. Hydrolytic fission of the dimeric quinoneimide leads to the formation of *o*-amino-xylenol, but the corresponding treatment of the methylated product gives small amounts of o-*dimethylamino*-s-m-*xylenol*, a colourless liquid, b. p. 154—156°/68 m.m., $d_4^{20\cdot6}$ 0·9955, d_4^{20} 0·996, $n_\alpha^{20\cdot6}$ 1·51811, $n_D^{20\cdot6}$ 1·52225, $n_\beta^{20\cdot6}$ 1·53437, $n_\gamma^{20\cdot6}$ 1·54476, n_D^{20} 1·5225 (*phenylurethane*, colourless, slender needles, m. p. 132—133°), which is also prepared by the action of methyl alcohol on *o*-aminoxylenol hydrochloride at 170—180°.

o-Amino-*s*-*m*-xylenol is smoothly converted by bromine in carbon disulphide solution into p-*bromo*-o-*amino*-s-m-*xylenol*, m. p. 136—138° (the *hydrobromide* is described), which is oxidised by air in alkaline solution to 4-*amino*-m-2 : 4-*xyloquinone*-2′-*bromo*-5′-*hydroxy*-m-4′-*xylylimide* (annexed formula), brownish-red plates, m. p. 99—120°. It is shown that the bromine atom enters the molecule of the amino-xylenol in the para-position to the hydroxyl group by the following series of experiments. The oxime of *o*-acetyl-*s*-*m*-xylenol is converted by bromine into the corresponding *p*-bromo-*compound*, slender, colourless needles, m. p. 188°, which when boiled with hydrochloric acid gives the bromoaminoxylenol, m. p. 136—138°; after removal of the amino-group, the latter gives *p*-bromo-*s*-*m*-xylenol, m. p. 116°, which is converted by nitric acid in glacial acetic acid solution into p-*bromo*-o-*nitro*-s-m-*xylenol*, colourless needles, m. p. 140—140·5° (the yellow sodium salt was prepared); on the other hand, *o*-amino-*s*-*m*-xylenol hydrochloride is transformed by treatment with sodium nitrite and cuprous bromide into o-*bromoxylenol*, b. p. 126°/33 mm., m. p. 54°.



The following derivatives of 5-bromo-*m*-cresol are described: 5-*bromo*-m-*tolyl methyl ether*, from the cresol and methyl sulphate, a colourless, highly refractive liquid, b. p. 139—140°/20 mm.; 4-*benzeneazo*-5-*bromo*-m-*cresol*, lustrous, ruby-red leaflets, m. p. 97—99°; *dibenzeneazo*-5-*bromo*-m-*cresol*, tile-red, lustrous prisms, m. p. 171—173°; 5-*bromo*-6-*acetyl*-m-*cresol*, coarse, glassy prisms, m. p. 50—52°, and its *semicarbazone*, colourless needles, m. p. 218—220°, and *oxime*, colourless, matted needles, m. p. 127°. The latter is converted by boiling hydrochloric acid into 5-*bromo*-6-*amino*-m-*cresol*, coarse, lustrous needles, m. p. 140—141° after previous darkening (*hydrochloride*, pearly leaflets, m. p. 140—141°), which is transformed by atmospheric oxidation in alkaline

solution into 3-*bromo*-4-*amino*-o-2 : 5-*toluquinone*-5′-*bromo*-3′-*hydroxy*-p-*tolylimide*, brownish-red platelets, m. p. 218—219°.

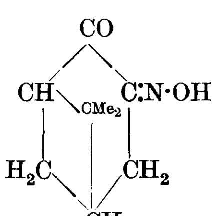
6-*Amino*-m-*cresol*, colourless needles, m. p. 157—159°, after previous softening (the *di-benzoyl* compound could not be obtained in the homogeneous state) is oxidised to 4-*amino*-m-2 : 5-*toluquinone*-3′-*hydroxy*-p-*tolylimide*, m. p. 185—186°, which is decomposed by hydrochloric acid with the formation of 6-amino-*m*-cresol; the dimeric quinoneimide gives an N-*acetyl* derivative, brownish-yellow, lustrous leaflets, m. p. 177—178°, and a *semicarbazone*, golden-yellow, lustrous needles, m. p. 195° (decomp.). H. W.

Epicamphor. II. WILLIAM HENRY PERKIN, jun., and ALAN FRANCIS TITLEY (T., 1921, **119**, 1089—1107).

Sesquiterpenes. I. Conversion of Cadinene into a Naphthalene Hydrocarbon. L. RUZICKA and JULES MEYER (*Helv. Chim. Acta*, 1921, **4**, 505—510).—Very little is at present known with regard to the carbon skeleton of the sesquiterpenes; the methods involved in their examination (oxidation, behaviour when exposed to high temperature) appear to the authors unsuitable for the investigation of a complicated group of substances which offer many points of attack. They therefore propose to examine dehydrogenation methods, and give an account of the behaviour of cadinene in these circumstances.

Cadinene, b. p. 134—136°/13 mm., is converted when heated with powdered sulphur at 200—265° into the *hydrocarbon*, $C_{15}H_{18}$, a colourless liquid, b. p. 157—158°/12 mm., or 291—292°/720 mm., d_4^{19} 0·9792, n_D^{19} 1·5851; it is free from sulphur and behaves as a saturated substance towards bromine in carbon disulphide solution and potassium permanganate. It gives a *picrate*, orange-yellow needles, m. p. 115°, a *styphnate*, yellow needles, m. p. 138°, and a *dihydride*, $C_{15}H_{20}$, a colourless liquid, b. p. 151—153°/12 mm.; the latter does not give a picrate. It is readily oxidised by cold dilute potassium permanganate solution. H. W.

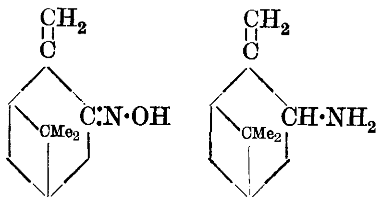
Pinene. III. Constitution of Nitrosopinene and its Transformation Products. L. RUZICKA and H. TREBLER (*Helv. Chim. Acta*, 1921, **4**, 566—574).—The formulæ ascribed previously to nitrosopinene and to pinylamine obtained from it by reduction with zinc and glacial acetic acid are not in accordance with Bredt's rule, since they are relatively stable substances. The authors have therefore been led to examine their behaviour towards ozone.



Nitrosopinene, m. p. 130°, gives an *ozonide* in carbon tetrachloride solution which is decomposed by water with the production of formic acid, formaldehyde, and oximinonopinone (annexed formula), which was characterised by its semicarbazone, m. p. 220° (decomp.), and oxime, m. p. 230°. Similarly, acetylpinylamine, m. p. 108°, when ozonised in glacial acetic acid solution, gives an acidic product from which a semicarbazone could not be

*y**

obtained and a neutral substance which is identified as α-acetylaminonopinone, m. p. 120—121°; the products obtained after treatment in carbon tetrachloride solution are formaldehyde, formic acid, a neutral substance which does not yield a semicarbazone, and an acid product which gives a *semicarbazone* (?) $C_{10}H_{17}O_3N_3$, m. p. 187—188°; the latter appears to be derived from a product of further degradation.



(I.) (II.)

It follows therefore that nitrosopinene (I) and pinylamine (II) and their transformation products are all derived from β-pinene. It is, however, known that pinylamine is convertible successively into pinocarveol and pinocarvone; the latter yields an oxime which is reducible to a primary amine and to these two compounds the structures I and II have been assigned previously. According to the authors, the oximes and the amines are geometrical isomerides, the difference being caused in the case of the oximes by the *cis*- or *trans*-position of the hydroxy-group to the methylene group and in that of the amines by the location of the amino-group on the one or the other side of the main plane with respect to the dimethylated carbon atom, 8. H. W.

Essential Oil of Dokudame. YEINOSUKE SHINOSAKI (*J. Chem. Ind. Japan*, 1921, **24**, 557—562).—By steam distillation of dokudame, *Houttuynia Cordata*, Thunb., a small quantity of a light brown oil of strong somewhat disagreeable odour was obtained. The main constituents were methyl *n*-nonyl ketone, an aliphatic terpene, probably myrcene, a cyclic terpene, and a solid acid.

K. K.

Essential Oil of Kokusagi. YEINOSUKE SHINOSAKI (*J. Chem. Ind. Japan*, 1921, **24**, 563—566).—By steam distillation of kokusagi, *Orixa Japonica*, Thunb., a small quantity of light brown oil of characteristic odour was obtained. The essential constituents were camphene, linalool, and some terpene alcohol and its ester.

K. K.

The Composition of French Oil of Turpentine and α-Pinene Bromide. PARISELLE (*Compt. rend.*, 1921, **172**, 1496—1499).—By careful fractional distillation in a vacuum of fifteen litres of French turpentine the author has obtained α-pinene and β-pinene separately and determined their physical constants. α-Pinene has b. p. 153·5—154·5°/760 mm.; 62°/32 mm.; d^0 0·8748; n_D^{13} 1·4690; $[\alpha]_D^{15}$ −43·48°; coefficient of viscosity η=0·0141. β-Pinene has b. p. 163—164°/760 mm.; 71·5°/34 mm.; d^0 0·8848; d^{15} 0·8728; n_D^{13} 1·479; $[\alpha]_D^{15}$ −19·80°; coefficient of viscosity η=0·0173. With hydrogen bromide, α-pinene gave a solid hydrobromide, m. p. 94°; b. p. 94°/12 mm.; $[\alpha]_D^{15}$ +27·95° and a liquid hydrobromide, b. p. 96°/12 mm. β-Pinene behaved similarly, giving the same com-

pounds. The action of bromine on α-pinene at low temperatures in carbon tetrachloride, even if hydrogen bromide is not liberated, results in a complex mixture of products of addition and substitution, the hydrogen bromide being absorbed by the pinene as fast as it is formed. The products isolated were a liquid monobromide, a crystalline dibromide, m. p. 150°, and Wallach's dibromide, m. p. 166—168°. W. G.

New Process for the Cold Vulcanisation of Caoutchouc. G. BRUNI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 280—283; *Giorn. Chim. Ind. Appl.*, 1921, **3**, 196—197).—Thiocarbanilide or other disubstituted aromatic thiocarbamide is formed in the mass of the material by the action of vaporised or dissolved carbon disulphide on an aromatic amine in presence of zinc or other oxide. [See *J. Soc. Chem. Ind.*, 1921, 520A.] T. H. P.

Thiouram Disulphides as Vulcanising Agents for Caoutchouc. E. ROMANI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 283—286; *Giorn. Chim. Ind. Appl.*, 1921, **3**, 197—199).—Tetraalkylthiouram disulphides are able to effect rapid vulcanisation of caoutchouc without addition of free sulphur, the action being rendered more energetic by the presence of zinc or other oxide. These disulphides, which are crystalline compounds, are obtained most readily by passing chlorine through aqueous solutions of dithiocarbamates of imines. Thus, for tetramethylthiouram disulphide, $2NMe_2{\cdot}CS{\cdot}S{\cdot}NH_2Me_2+2Cl \longrightarrow NMe_2{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}NMe_2+2NHMe_2,HCl$; the imine hydrochloride may be used for the preparation of fresh dithiocarbamate. [Compare *J. Soc. Chem. Ind.*, 1921, 520A.] T. H. P.

Picrotoxin. II. Behaviour of the Bromopicrotoxinins toward Concentrated Halogen Acids. PAUL HORRMANN and WOLFRAM BEHSCHNIDT (*Arch. Pharm.*, 1921, **259**, 69—93).—The reaction has been investigated previously by Sielisch (A., 1912, i, 886), who, however, did not start with a uniform material, since Horrmann (A., 1912, i, 709) has shown that Meyer and Bruger's bromopicrotoxinin (A., 1899, i, 226) is a mixture of α- and β-isomerides. The work has therefore been repeated and extended. It is shown that the individuality of the bromopicrotoxinins is exhibited in all their derivatives, even to such as result from oxidation with nitric acid; the same halogen-free products, however, are obtained from either series when the halogen is replaced by hydrogen.

β-Bromopicrotoxinin is converted by boiling concentrated hydrochloric acid or, more advantageously, by protracted treatment with the reagent at the atmospheric temperature into hydroxy-β-bromopicrotoxinic acid, $C_{15}H_{19}O_8Br$, decomp. 208° (hydrated), 225° (anhydrous), $[\alpha]_D^{15}$ −71° 23′ in aqueous solution (Sielisch, *loc. cit.*, gives decomp. 223°). The *methyl* ester, $C_{16}H_{21}O_8Br,H_2O$, has m. p. 220°, $[\alpha]_D^{15}$ (anhydrous) +69° 29′ in aqueous solution, whereas the *ethyl* ester ($+3H_2O$) decomposes at 230° and (anhydrous) has $[\alpha]_D^{15}$ −82° 33′ when dissolved in water. *Hydroxy-α-bromopicrotoxinic acid*, decomp. 228° $[\alpha]_D^{17}$ −58° 2′ in aqueous solution, is

obtained similarly from α-bromopicrotoxinin and cold concentrated hydrochloric acid.

β-Bromopicrotoxinin is slowly converted by hydrobromic acid at the atmospheric temperature into a mixture of dibromopicrotoxinic acid, $C_{14}H_{17}O_5Br_2\cdot CO_2H,H_2O$, decomp. 278° (compare Sielisch, *loc. cit.*) and hydroxy-β-bromopicrotoxinic acid. The former is also prepared from β-bromopicrotoxinic acid by the regulated action of boiling hydrobromic acid; the pure substance is scarcely affected by boiling water or boiling hydrobromic acid. α-Bromopicrotoxinic acid dissolves readily in hot hydrobromic acid; a considerable portion rapidly separates unchanged from the hot solution, but a homogeneous material could not be isolated from the remainder. Neither the α- nor the β-bromo-acid is affected by boiling dilute sulphuric acid (20%).

α-Bromopicrotoxinin is oxidised by concentrated nitric acid to a *dicarboxylic acid*, $C_{13}H_{15}O_7Br,4H_2O$, needles, decomp. 170° $[\alpha]_D^{15}-72° 1'$ (anhydrous) in aqueous solution, whereas β-bromopicrotoxinin yields an isomeric *dicarboxylic* acid, $C_{13}H_5O_7Br,2H_2O$, decomp. 184°, $[\alpha]_D^{15}-53° 4'$, for the anhydrous acid when dissolved in water; the latter substance is similarly prepared from hydroxy-β-bromopicrotoxinic acid (compare Sielisch, *loc. cit.*). It is not affected when heated above its melting point. Its alcoholic hydroxyl group is unchanged by treatment with thionyl chloride at 100°.

α- and β-Bromohydroxypicrotoxinic acids are transformed by zinc dust and ammonium chloride in aqueous alcoholic solution into picrotoxinolactone, $C_{15}H_{18}O_7,H_2O$, m. p. 298° (decomp.). Similar treatment of β-dibromopicrotoxinic acid leads to the formation of *dihydro-β-picrotoxinic acid*, $C_{15}H_{20}O_7,H_2O$, needles, decomp. 210°, $[\alpha]_D^{15}-8° 23'$ (anhydrous) in absolute alcoholic solution (*ethyl* ester, $C_{17}H_{24}O_7,H_2O$, needles, decomp. 180°). Attempts to remove the bromine atoms from β-bromopicrotoxinindicarboxylic acid by zinc dust and ammonium chloride or acetic acid did not lead to definite results. H. W.

Tannins and Similar Substances. VII. Stereoisomeric Catechins. KARL FREUDENBERG, OTTO BÖHME, and ALFRED BECKENDORF (*Ber.*, 1921, **54**, [*B*], 1204—1213).—It has been shown previously (A., 1920, i, 752) that Gambier catechin is a derivative of pentamethoxy-αγ-diphenylpropane, and a similar series of experiments now proves that acacatechin (Perkin, P., 1904, **20**, 172) is directly related to the same substance. The optical behaviour of the acetyl and benzoyl derivatives of these catechins indicates strongly that they are stereochemically related, Gambier catechin being a homogeneous dextrorotatory form and acacatechin a mixture of the racemic and lævorotatory compounds; it is quite possible that the pure *l*-form occurs in acacia catechin and that partial racemisation occurs during the extraction process, which is necessarily more drastic than in the case of the Gambier variety. Since catechin contains two asymmetric carbon atoms, further stereoisomerides are to be expected, of which catechin-*C* of Perkin and Yoshitake (T., 1902, **81**, 1160) is probably an example.

Acacatechin is treated with methyl sulphate and the crude tetramethyl derivative is reduced and methylated according to the method of von Kostanecki and Lampe (A., 1907, i, 334), yielding thereby 2 : 4 : 6 : 3′ : 4′-pentamethoxy-$\alpha\gamma$-diphenylpropane, m. p. 87—88° (corr.), which is identical in all respects with the synthetic product.

Gambier catechin is converted by acetic anhydride in the presence of pyridine into the penta-acetate, m. p. 132°, $[\alpha]_D^{17}+40{\cdot}6°$ in *s*-tetrachloroethane solution; the process gives no evidence of the presence of an isomeric substance in the material. Acacatechin, on the other hand, yields a lævorotatory penta-acetate from which r-*pentaacetylacacatechin*, m. p. 165°, can be isolated after repeated crystallisation. If the crude lævorotatory acetate is mixed with the calculated quantity of Gambier catechin penta-acetate, the *r*-derivative is obtained in theoretical amount. Similarly, Gambier catechin pentabenzoate (compare Perkin and Yoshitake, *loc. cit.*) has m. p. 170—172°, $[\alpha]_D^{18}+55{\cdot}4°$ ($\pm 0{\cdot}5°$) in *s*-tetrachloroethane, whilst the product from acacatechin has $[\alpha]_D-19°$, and after admixture with the requisite quantity of the Gambier derivative yields r-*catechin pentabenzoate*, m. p. 185°.

d-Catechin (Gambier catechin) has ($+4H_2O$) m. p. about 95° (anhydrous), m. p. about 177°, $[\alpha]_D^{17-18°}-0{\cdot}47°$ ($\pm 0{\cdot}03°$) in alcohol (96%), $+3{\cdot}7°$ ($\pm 0{\cdot}5°$) in alcohol (50%), $+11{\cdot}0°$ ($\pm 0{\cdot}6°$) in commercial acetone, $+17{\cdot}1°$ ($\pm 0{\cdot}5°$) in commercial acetone (50%), $+18{\cdot}4°$ ($\pm 0{\cdot}09°$) in water. *dl*-Catechin has ($+3H_2O$) m. p. 216—218° (decomp.) after softening above 100° (anhydrous), m. p. 216—218° (decomp.). H. W.

Catechin. KARL FREUDENBERG (*Zeitsch. angew. Chem.*, 1921, **34**, 247—248).—The author briefly summarises the present knowledge of the chemistry of catechin, together with some original observations of his own. The identity of Kostanecki's methylated reduction product of catechin, the corresponding product from acacatechin, and synthetic pentamethoxy-α-γ-diphenylpropane on which doubt has been cast by Nierenstein (T., 1920, **117**, 971, 1151) has now been further established by an absolute identity of melting points, and also by crystallographic measurements. The optical activity of the catechins is established, and it is shown that catechin and acacatechin are optical isomerides, the former being *d*-catechin, and the latter a mixture of *l*-catechin with *dl*-catechin. From acacatechin a racemic acetyl compound of high melting point was isolated, and the same compound was obtained by mixing together the acetyl derivatives of catechin and acacatechin in the requisite proportions. It is suggested that the acacatechin originally present in acacia is pure *l*-catechin, and that partial racemisation occurs during extraction. A similar partial racemisation was observed during the prolonged boiling of an aqueous solution of *d*-catechin, and this is accompanied by the formation of the second theoretically possible racemate, which was eventually isolated in a pure state by the transformation of the synthetically prepared *dl*-catechin above mentioned. G. F. M.

New Method for the Preparation of Coumarandiones. R. Stollé and E. Knebel (*Ber.*, 1921, **54**, [*B*], 1213—1220).—Aryloxalyl chlorides are readily obtained by the action of an excess of oxalyl chloride on phenols and, as far as the present experiments indicate, can be distilled under diminished pressure without decomposition. Under the influence of aluminium chloride in carbon disulphide solution, phenyloxalyl chloride gives salicylic acid and a little *o*-hydroxyphenylglyoxylic acid; experiments with other aryloxalyl chlorides show that the yield of *o*-hydroxyphenylglyoxylic acids or coumarandiones improves with increasing stability of the latter, which is increased by the presence of substituents in the meta-position but diminished by those in the ortho- or para-positions.

Phenyloxalyl chloride, OPh·CO·CO·Cl, has b. p. 97°/12 mm., m. p. 57° (corresponding *anilide*, needles, m. p. 137°, p-*toluidide*, lustrous needles, m. p. 155°). p-*Tolyloxalyl chloride*, a yellow liquid which solidifies when cooled, b. p. 115°/13 mm. (*anilide*, needles, m. p. 132°), gives mainly *p*-cresotic acid, together with a little 5-methyl-*o*-hydroxyphenylglyoxylic acid. m-*Tolyloxalyl chloride*, a pale yellow oil, b. p. 120°/14 mm. (*anilide*, m. p. 94°), yields chiefly 6-methylcoumarandione and relatively little *m*-cresotic acid. s-m-*Xylyloxalyl chloride*, a yellow liquid, b. p. 128°/12 mm. (*anilide*, lustrous leaflets, m. p. 113°), gives a 90% yield of 4 : 6-*dimethylcoumarandione*, long, yellow needles, m. p. 144. The latter condenses with β-oxythionaphthen in glacial acetic acid solution with the formation of the *substance* $\begin{array}{l}C_6H_2Me_2\\ | \\ O{-}{-}{-}CO\end{array}>C:C<\begin{array}{l}S\\CO\end{array}>C_6H_4$, red, silky needles, m. p. 225°, with indoxyl to give the *compound*, $\begin{array}{l}C_6H_2Me_2\\ | \\ O{-}{-}{-}CO\end{array}>C:C<\begin{array}{l}NH\\CO\end{array}>C_6H_4$, dark violet-brown needles, m. p. 255°, and with 4 : 6-dimethylcoumaranone to yield the *product* (?) $\begin{array}{l}C_6H_2Me_2\\ | \\ O{-}{-}{-}CO\end{array}>C:C<\begin{array}{l}O\\CO\end{array}>C_6H_2Me_2$, pale yellow needles, m. p. 233°, which is converted by warm alcoholic potassium hydroxide solution into a *substance*, red, rhombic leaflets, m. p. 218°.

p-*Chloro*-s-m-*xylyloxalyl chloride*, b. p. 157°/13 mm., m. p. 51° (corresponding normal *ester*, needles, m. p. 156°, *anilide*, m. p. 160°), is transformed by aluminium chloride into 5-*chloro*-4 : 6-*dimethylcoumarandione*, lustrous, yellow needles, m. p. 121°. It is oxidised by hydrogen peroxide in alkaline solution to 5-*chloro*-o-*hydroxy*-4 : 6-*dimethylbenzoic acid*, long needles, m. p. 193°. It condenses readily with indoxyl in glacial acetic acid solution in the presence of concentrated hydrochloric acid, giving the *substance*

$$\begin{array}{l}C_6HMe_2Cl\\ | \\ O{-}{-}{-}{-}CO\end{array}>C:C<\begin{array}{l}NH\\CO\end{array}>C_6H_4,$$

dark violet-brown needles, m. p. about 305° (decomp.).

p-*Xylyloxalyl chloride*, a pale yellow liquid, b. p. 124°/14 mm. (*anilide*, lustrous leaflets, m. p. 120°), is transformed in good yield into 4 : 7-*dimethylcoumarandione*, yellow prisms, m. p. 136°.

H. W.

The Halogenation of Thiophen by means of Acetylchloroamide and Acetylbromoamide. WILHELM STEINKOPF and ANNEMARIE OTTO (*Annalen*, 1921, **424**, 61—71).—Wohl's method of halogenation (A., 1919, i, 198) has been applied to thiophen, and 2-chlorothiophen, 2 : 5-dichlorothiophen, 2-bromothiophen, and 2 : 5-dibromothiophen have been produced by this means.

The relation of thiophen to aromatic substances on the one hand and to olefinic compounds on the other is discussed in the light of these and other known facts. C. K. I.

Thiophen Series. X. The Preparation and Reduction of Thienyl Ketones. WILHELM STEINKOPF and ILSE SCHUBART (*Annalen*, 1921, **424**, 1—23. Compare A., 1917, i, 278).—The formation of ketones from cyclic substances by the action of acyl chlorides in the presence of phosphoric oxide proceeds fairly smoothly in the thiophen series, condensation taking place in one of the positions adjacent to the sulphur atom unless both these are already occupied; in this case the acyl residue enters into one of the remaining positions, although with less readiness.

The reduction of the carbonyl groups in these products to methylene residues by the action of amalgamated zinc and hydrochloric acid affords a general method for the introduction of alkyl groups into the thiophen nucleus.

The following individual substances are described: 2-*Thienyl ethyl ketone*, a pale yellow oil, b. p. 100—101°/11 mm., *semicarbazone*, white leaflets, m. p. 167°; the *aminoguanidone*,

$$C_4SH_3\cdot CEt{:}N\cdot NH\cdot C(NH)\cdot NH_2,$$

was isolated as its *picrate*, $C_8H_{12}N_4S,C_6H_3O_7N_3$, yellow needles, m. p. 215°. 2-*Thienyl propyl ketone*, b. p. 118—121°/16 mm., forming an *oxime*, needles, m. p. 57°, and a *semicarbazone*, needles, m. p. 176—176·5°. 2-*Thienyl* iso*butyl ketone*, a colourless liquid, b. p. 130·5—135°/22 mm., forming an *oxime*, m. p. 88°, which is converted by treatment with chloral in benzene into an unstable isomeric *oxime*, m. p. 102°; the *semicarbazone* forms needles, m. p. 168—169°, the *aminoguanidone*, $C_4SH_3\cdot C(CH_2Pr^{\beta}){:}N\cdot NH\cdot C(NH)\cdot NH_2$, has m. p. 98—99°, and its *picrate* m. p. 212°; the *p*-phenetidide has m. p. 51—53°. 5-Methyl-2-thienyl methyl ketone yields a *semicarbazone*, m. p. 225° (decomp.). 2 : 5-*Dimethyl-2-thienyl methyl ketone* has b. p. 125—126°/28 mm.; the *semicarbazone* forms white needles, m. p. 213°. 2-iso*Amylthiophen* is a colourless oil of unpleasant odour, b. p. 74—75°/11 mm. 2-*Methyl-5-ethylthiophen* has b. p. 53—55°/22 mm. 2-o-*Methylbenzylthiophen*, $C_4SH_3\cdot CH_2\cdot C_6H_4Me$, is liquid, b. p. 140—145°/13 mm. C. K. I.

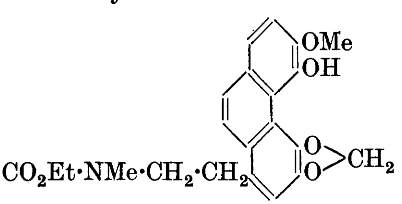
The Action of Ethyl Chloroformate on Tertiary Cyclic Amines [Alkaloids]. J. GADAMER and FRIEDA KNOCH (*Arch. Pharm.*, 1921, **259**, 135—158).—Ethyl chloroformate has been used extensively by Fischer and his co-workers for the protection of hydroxyl groups in the preparation of the chlorides of phenolcarboxylic acids. Attempts to apply it in a similar manner in the cases of alkaloids have shown that the substance behaves in quite a different way, its action here being similar to, but weaker than, that of

cyanogen bromide. The latter causes the fission of the dihydro-*iso*indole and tetrahydro*iso*quinoline, pyrrolidine, piperidine, and tetrahydroquinoline rings (in order of increasing difficulty), whereas ethyl chloroformate readily attacks the tetrahydro*iso*quinoline ring and is almost without action towards the remaining systems.

In general, the experiments are performed by agitating a solution of the material under investigation in ether or chloroform with ethyl chloroformate and aqueous alkali hydroxide, the proportions used being one, four, and seven molecules respectively. Initially, only two and three molecular proportions of the chloroformate and alkali are used, the remainder being added after the odour of the ester has disappeared. Agitation is continued until the ether or chloroform layer remains clear on standing, which is usually the case after about two hours. The basic and neutral products are separated by agitation of the ethereal or chloroform solution with dilute acid.

N-Phenylpiperidine and tropine are scarcely affected by ethyl chloroformate.

Bulbocapnine (Gadamer and Kuntze, A., 1911, i, 1012) is almost quantitatively converted at the atmospheric temperature or at 0° into *ethyl bulbocapninecarboxylate*, m. p. 152—153°, mixed with a small amount of *ethyl bulbocapninedicarboxylate*, m. p. 137—138°. The neutrality of both products indicates that reaction has occurred at the nitrogen atom, and this is supported by the observation that the hydroxyl group, which was expected to be the point of attack, remains intact in the monocarboxylate compound. Fission of the ring can occur theoretically in two possible directions (as is actually the case in Hofmann's process), but in this instance the exclusive formation of the substance (annexed formula) is shown by the observation that the product is immediately and completely inactive optically. Further evidence that the reagent primarily attacks the nitrogen atom is afforded by the demonstration that bulbocapnine methyl ether is transformed with the same readiness into *ethyl bulbocapninecarboxylate methyl ether*, coarse needles, m. p. 95—96°, whilst the possibility of attributing the indifference of the hydroxyl group of bulbocapnine to the effect of steric hindrance is excluded by the observation that corydine, in which the hydroxyl group is much less protected, yields almost quantitatively *ethyl corydinecarboxylate*, m. p. 117—118°. The firmness with which the carbethoxy-group is retained in these products is remarkable, and it has not been found possible to secure conditions under which it can be removed by hydrolysis without extensive decomposition of the remainder of the molecule. *r*-Laudanosine yields *ethyl* r-*laudanosinecarboxylate*, colourless needles, m. p. 156—157°; the same substance is ultimately obtained from *l*-laudanosine, but the observation of transient optical activity (dextrorotation) shows the intermediate production of the additive



chloro-compound, which, however, is too unstable to allow of its isolation.

Pyridine and ethyl chloroformate yield a very unstable additive *compound* which decomposes into pyridine hydrochloride, ethochloride, and carbon dioxide (compare Hopkins, T., 1920, **117**, 278). Papaverine is only slightly attacked, yielding probably *ethyl*iso-*papaverinecarboxylate* mixed with large quantities of unchanged alkaloid.

Morphine yields a small amount of a neutral *substance*, $C_{17}H_{16}O_4N(CO_2Et)_3$, $[\alpha]_D -188\cdot8°$, in alcoholic solution, but is mainly transformed into ethyl morphinecarboxylate, m. p. 123—124°, $[\alpha]_D -143\cdot7°$ in alcoholic solution, which is purified through the *hydrogen tartrate*, which softens at about 121—122° and has $[\alpha]_D -51\cdot4°$ in water. Reaction occurs at the phenolic hydroxyl group, but attempts to obtain the dicarbethoxy-compound were unavailing. Codeine likewise undergoes ring fission to only a very slight extent, the main product of the action being *ethyl codeinecarboxylate*, flat, transparent crystals, m. p. 77—78°, $[\alpha]_D -202\cdot8°$ in alcoholic solution [*hydrogen tartrate*, slender, opaque needles, m. p. 120° (decomp.) which rises to 137—140° when the substance is exposed to air; $[\alpha]_D -120\cdot3°$ in aqueous solution]. Thebaine, on the other hand, suffers quantitative ring fission, but the product of the action is so unstable that its isolation is impossible. The behaviour of the three alkaloids towards ethyl chloroformate and cyanogen bromide respectively is thus precisely similar. Heroine yields about 10% of neutral material, but the remainder is not unchanged alkaloid.

Chelidonine reacts readily with ethyl chloroformate, giving a 70% yield of optically inactive *ethyl anhydrochelidoninecarboxylate*, colourless crystals, m. p. 97—98°, a molecule of water being eliminated during the reaction. The same substance is obtained from *O*-acetyl and *O*-benzoyl-chelidonine, but the intermediate formation of an unstable substance of opposite sign of rotation could not be established. It appears probable that the production of a new benzene nucleus is involved in the formation of the anhydro-compound, and this view is supported by the apparently saturated nature of the substance. H. W.

Cinchona Alkaloids. IV. Transformations of the Diazonium Compounds of 5-Aminocupreine and 5-Aminohydrocupreine and their Methyl and Ethyl Ethers. Formation of Diazoanhydrides and of Cuprean and Hydrocuprean and their Ethers. β-Ethylcupreine. G. Giemsa and J. Halberkann (*Ber.*, 1921, **54**, [*B*], 1167—1189. Compare A., 1919, i, 342; 1920, i, 496).—Attempts to prepare the 5-hydroxy-cinchona alkaloids by the action of boiling water on the diazonium compounds have shown the latter to be abnormal in their reactions. When preserved in cold solution for some hours, the ability to couple with β-naphthol is gradually lost, but nitrogen is not evolved, the product being a diazo-anhydride; in both the cupreine and hydrocupreine series, the same product is obtained whether the phenol

or its methyl or ethyl ether is used. When the diazo-anhydrides are boiled in acid or alkaline solution, nitrogen is eliminated and the alcoholic group is reduced, the products being termed cuprean and hydrocuprean respectively. The mechanism of the process is not fully elucidated, but it appears most probable that the reduction of one molecule is effected at the expense of the oxidation of a second molecule, thus accounting in some measure for the poverty of yield of the reduced compounds. It is, however, established that the formation of the anhydride is the primary, and reduction the secondary process in hot solution. In the cases of the ethers, it is possible to reverse this order since, when the freshly-prepared diazonium solutions are heated with copper paste, nitrogen is vigorously evolved and ethers of cuprean or hydrocuprean are obtained.

Heidelberger and Jacobs (A., 1920, i, 634) have suggested that in place of the prefix "deoxy" the suffix "an" should be used, for example, in place of deoxyquinine they would use quinan. The authors object to the alteration on historical grounds and because of the widespread use of the term "deoxy" to denote the reduction of the alcoholic to the paraffin group.

Hydrocuprean, $C_{19}H_{24}ON_2$, colourless, irregularly rectangular leaflets or plates, m. p. 173°, $[\alpha]_D^{20}$ +90·0° in alcohol, +97·5° in ether, is prepared by rapidly diazotising aminoethylhydrocupreine and heating the solution after addition of sulphuric acid and sodium sulphate at 85—90° until a portion of it no longer couples with an alkaline solution of β-naphthol. (The corresponding *monohydrate*, coarse, colourless prisms, m. p. 134°, is obtained by crystallisation of the substance from dilute alcohol or acetone.) It is extensively associated when dissolved in nitrobenzene or naphthalene, but has normal molecular weight in freezing aniline. The *hydrochloride*, $C_{19}H_{24}ON_2,2HCl$, leaflets, m. p. 191—192°, after softening at about 185°, and the *platinichloride*, rectangular leaflets, decomp. 290°, are described. The preparation of hydrocuprean from aminohydroquinine and (in poorer yield) from aminohydrocupreine is outlined. *Ethylhydrocuprean*, an almost colourless, viscous liquid, $[\alpha]_D^{20}$ +77·7° in alcoholic, +77·8° in ethereal solution (*platinichloride*, reddish-yellow powder, incipient decomp. about 250°), is prepared by treating hydrocuprean with a solution of sodium in alcohol and ethyl *p*-toluenesulphonate, and is reconverted into the phenol by concentrated hydrochloric acid at 145°. Its direct preparation from diazotised aminoethylhydrocupreine by means of copper powder is also described. *Methylhydrocuprean* [*hydroquinan*], an almost colourless liquid, $[\alpha]_D^{20}$ + 81·7° in alcoholic solution, is obtained by alkylation of the corresponding phenol with diazomethane, but to a slight extent only with methyl sulphate or methyl toluene-*p*-sulphonate, or by the action of copper powder on diazotised aminohydroquinine.

If the diazotised solution of aminoethylhydrocupreine is preserved for some time, the diazonium compound becomes converted into *hydrocupreine-5-diazoanhydride*, brownish-yellow to golden-yellow, triangular leaflets, decomp. 120—200°, $[\alpha]_D^{20}$ +92·4° in

alcoholic, $-23 \cdot 9°$ in ethereal solution; the change is more rapid if it is placed under greatly diminished pressure or rendered alkaline. The normal *hydrochloride* crystallises in long, pale-yellow needles. It is transformed into hydrocuprean by hot dilute sulphuric acid or by catalytic reduction with hydrogen in the presence of nickel and aqueous sulphuric acid or palladium and alcohol. *Cupreine-5-diazoanhydride*, golden-yellow leaflets or needles, decomp. 145—146° after darkening at 120°, $[\alpha]_D^{20}$ $+89 \cdot 5°$, in absolute alcoholic, $19 \cdot 3°$ in ethereal solution, is similarly prepared from aminocupreine, aminoquinine, or aminocupreine ethyl ether.

Cuprean, $C_{19}H_{22}ON_2$, small, colourless needles, m. p. 206°, $[\alpha]_D^{20}$ $+82 \cdot 8°$ in absolute alcoholic solution, is preferably prepared by the gradual addition of sulphuric acid (5%) to a boiling aqueous solution of the corresponding diazo-anhydride. Much less satisfactory results are obtained by the addition of copper powder to freshly-diazotised aminocupreine, since the reaction in this case is largely restricted by the formation of the diazo-anhydride, which is stable under these conditions. It is converted by diazomethane into *methylcuprean* (*quinan*), a nearly colourless oil, which solidifies when cooled, $[\alpha]_D^{20}$ $+70 \cdot 1°$ in absolute alcohol, and by ethyl sulphate or ethyl toluene-*p*-sulphonate into *ethylcuprean*, a yellow liquid, $[\alpha]_D^{20}$ $+66 \cdot 5°$, when dissolved in absolute alcohol.

The decomposition of freshly-diazotised solutions of aminoethylcupreine by copper powder leads to the production of ethylcuprean and relatively smaller amounts of β-*ethylcupreine*, small, colourless, quadratic crystals, m. p. 164—165°, $[\alpha]_D^{20}$ $-52 \cdot 8°$ in absolute alcoholic solution. Reduction and hydrolysis of the latter give hydrocuprean. H. W.

Cinchona Alkaloids. V. Stereoisomeric Compounds of Hydrocuprean. G. Giemsa and J. Halberkann (*Ber.*, 1921, **54**, [*B*], 1189—1204. Compare preceding abstract).—Numerous experiments are described which owed their origin to the desire to prepare hydrocuprean by other methods and to establish its identity with certainty; this, however, has not been accomplished.

The chlorides mentioned below were prepared by the action of phosphorus pentachloride on the boiling solution of the alkaloid in chloroform, the quinenes and their homologues and isologues by heating the chlorides with alcoholic potassium hydroxide solution and the deoxy-compounds by the action of iron and dilute sulphuric acid on the chloro-derivatives (compare Koenigs, *Ber.*, 1895, **28**, 347; 1896, **29**, 372). The following individuals are described: chloroquinine, $[\alpha]_D^{20}$ $+62 \cdot 6°$ in alcoholic solution. Quinene ($+2H_2O$), m. p. about 67°, then resolidifying and having m. p. 90—91°, $[\alpha]_D^{20}$ $+52 \cdot 5°$ (anhydrous substance) in absolute alcoholic solution (dihydrochloride, needles, m. p. 182°; Heidelberger and Jacobs, A., 1920, i, 634, give m. p. 180—185°). *Chloroethylcupreine*, colourless prisms, m. p. 130°, $[\alpha]_D^{20}$ $+55 \cdot 5°$ and $56 \cdot 2°$ in absolute alcohol ($c=2 \cdot 2892$ and $1 \cdot 0404$). *Ethylcupreene*, almost colourless liquid, $[\alpha]_D^{20}$ $+36 \cdot 5°$ in alcoholic solution. *Cupreene*, $C_{19}H_{20}ON_2$, almost colourless resin, m. p. about 110° after softening at about 85°, $[\alpha]_D^{20}$ $+11 \cdot 8°$ in

alcohol. Chlorohydroquinine, m. p. 144°, $[\alpha]_D^{20}$ +43·0° in absolute alcohol (Heidelberger and Jacobs give m. p. 143—144°, $[\alpha]_D$ +42·1°). *Hydroquinene*, needles (+$2H_2O$), anhydrous, m. p. 78—79°, $[\alpha]_D^{20}$ +29·5° in alcohol; *dihydrochloride*, slender, dark-yellow needles, m. p. 209°. *Chloroethylhydrocupreine*, colourless, prismatic rods, m. p. 147°, $[\alpha]_D^{23}$ +37·7° and +37·2° in absolute alcoholic solution (c=0·8484 and 2·6644). *Ethylhydrocupreene*, a yellow liquid, $[\alpha]_D^{20}$ +29·8° in absolute alcohol. *Hydrocupreene* (by dealkylation of hydroquinene or ethylhydrocupreene by hydrochloric acid at 145—150°), m. p. 85—86° (+$2H_2O$), 155° after contracting from 65° (anhydrous), $[\alpha]_D^{20}$ +27·1° in alcoholic solution; *dihydrochloride*, yellow crystals (+$3H_2O$), anhydrous, m. p. 167°, after softening above 150°. Deoxyquinine, m. p. 51—52° (for the dihydrate), [Koenigs, *loc. cit.*, and Rabe (A., 1910, i, 417), give m. p. 51—52° and 48° respectively], m. p. 94° (anhydrous), $[\alpha]_D^{20}$ −89·4° (hydrated), −99·9° and −99·6° (anhydrous) in absolute alcoholic solution (c=0·9128 and 1·6175): *dihydrochloride*, needles, m. p. about 130°. *Deoxyethylcupreine*, yellow oil, $[\alpha]_D^{20}$ −98·5° in alcoholic solution. Deoxycupreine could not be obtained by dealkylation of deoxyquinine or deoxyethylcupreine. Deoxyhydroquinine (+$2H_2O$), m. p. 68—69° after softening at 61°, $[\alpha]_D^{20}$ −80·15° in alcoholic solution (Heidelberger and Jacobs give $[\alpha]_D$ −77·5°), *dihydrochloride*, long, colourless needles. *Deoxyethylhydrocupreine*, pale yellow liquid, $[\alpha]_D^{20}$ −85·6° in absolute alcohol. Deoxyhydrocupreine, m. p. 182°, $[\alpha]_D^{20}$ −79·1° and −80·2° in alcohol (c=1·2324 and 1·7200), whereas Heidelberger and Jacobs give m. p. 191—191·5°, $[\alpha]_D$ −77·1° (c=0·973). Deoxyquinidine (+$2H_2O$), m. p. 82°, $[\alpha]_D^{20}$ (hydrated) +174·4°, (anhydrous) +194·2° in alcoholic solution whereas Rabe (*loc. cit.*) gives +211·1° (anhydrous). Hydroquinidine, m. p. (anhydrous) 167—168°, $[\alpha]_D^{20}$ +231·3° and 230·4° in absolute alcohol (c=2·0216 and 2·6304), $[\alpha]_D^{20}$ +233·6° in a mixture of alcohol 96% (1 vol.) and chloroform (2 vols.), whereas Irschick (Diss. Jena, 1913), found $[\alpha]_D^{15}$ +237·5° in absolute alcohol (c=0·4); the sulphate crystallises above 20° in needles consisting of the trihydrate, below 10° in prisms containing $18H_2O$, a portion of which is readily lost on exposure to air. Chlorohydroquinidine, a brown resin (according to Heidelberger and Jacobs, plates, m. p. 93·5—95°), which is converted by further treatment with phosphorus pentachloride and chloroform into (?) *dichlorohydroquinidine*, m. p. 191°. Deoxyhydroquinidine (+$2H_2O$), m. p. 72—73°, $[\alpha]_D^{20}$ +133·6° in alcoholic solution, whereas Heidelberger and Jacobs give m. p. 81—83°, $[\alpha]_D^{22·5}$ +167·3°. Deoxyhydrocupreidine, flat needles, m. p. 176—177°, $[\alpha]_D^{20}$ +151·0° in absolute alcohol, whereas Heidelberger and Jacobs give m. p. 183—183·5°, $[\alpha]_D^{24}$ +183·7° (*dihydrate*, pointed needles, m. p. 97°). H. W.

Synthetic Investigations in the Quinine Series. II. Quinine-like Compounds. L. RUZICKA (*Helv. Chim. Acta*, 1921, **4**, 482—485).—The synthesis of 4-methyl-3-ethylpyridine (A., 1919, i, 550) is the last link in a chain of reactions which should lead to the complete synthesis of the dihydrocinchona alkaloids,

the completion of which is only delayed by the unattained fission of *r*-homocincholeupone (Koenigs and Ottmann, this vol., i, 595) into its optically active components.

The recent synthetic work of Kaufmann and Rabe (A., 1913, i, 763), Rabe, Pasternack and Kindler (A., 1917, i, 283), on the one hand, and of Karrer (A., 1918, i, 38), on the other, has led to the preparation of compounds of the types

$$C_9NH_6\cdot CH(OH)\cdot CH_2\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$$

and $C_9NH_6\cdot CH(OH)\cdot CH<\begin{matrix}NH\cdot CH\\ CH-CH\end{matrix}$ respectively. The former of these differs from the typical cinchona alkaloids, since the carbon atom between the nitrogen atom and the carbinol group is not nuclear, whilst, although this is the case in the latter compound, the aromatic nature of the pyrrole ring is not equivalent to that of the hydrogenated quinuclidine ring. The author therefore outlines his intention of synthesising compounds of the type,

$$C_9NH_6\cdot CH(OH)\cdot CH<\begin{matrix}NMe\cdot CH_2\\ CH_2-CH_2\end{matrix}$$

and $C_9NH_6\cdot CH(OH)\cdot CH<\begin{matrix}NMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>CH_2$, which fulfil the main characteristics of the quinuclidine ring, namely, a hydrogenated system with strongly basic properties and nuclear position of the uniting carbon atom. The author proposes to designate substances of this class as "monocyclic cinchona alkaloids." H. W.

Synthetic Investigations in the Quinine Series. III. Aliphatic Quinatoxins. L. Ruzicka [and, in part, C. T. Seidel] (*Helv. Chim. Acta*, 1921, **4**, 486—505. Compare preceding abstract).—The esters of quinolinecarboxylic acids are condensed with methyl-2-piperidone and allied compounds (Ruzicka, this vol., i, 591) to yield compounds which are hydrolysed by hydrochloric acid with loss of carbon dioxide and formation of aliphatic quinatoxins, thus:

$$C_9NH_6\cdot CO_2Et + CH_2<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot NMe\end{matrix}>CH_2 \longrightarrow$$

$$\underset{\text{(I.)}}{C_9NH_6\cdot CO\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot NMe\end{matrix}>CH_2} \longrightarrow$$

$$\underset{\text{(II.)}}{C_9NH_6\cdot CO\cdot CH(CO_2Et)\cdot [CH_2]_3\cdot NHMe} \longrightarrow C_9NH_6\cdot CO\cdot [CH_2]_4\cdot NHMe.$$

The latter substances are transformed by bromine and subsequent elimination of hydrogen bromide into monocyclic quinaketones.

The yield of primary condensation product reaches 55—60% in the case of the alkyl-2-piperidones, but only about 20% with the ε-aminolactams. Subsidiary products are not formed in appreciable amount and unused material can generally be recovered readily. The condensation, like the more usual acetoacetic ester synthesis, appears therefore to be a balanced action.

Ethyl quinoline-4-carboxylate condenses with methyl-2-piperidone in light petroleum solution in the presence of powdered sodium ethoxide to *4-quinolyl-3-N-methyl-2-piperidonyl ketone* (I), almost colourless, monoclinic prisms, m. p. 95° [*picrate*, pale yellowish-brown leaflets, m. p. 207° (decomp.)]. It is converted by concentrated hydrochloric acid into *4-quinolyl δ-methylaminobutyl ketone* (II), viscous, pale yellowish-brown liquid which slowly darkens and resinifies on exposure to air and very gradually becomes partly crystalline after long preservation in a sealed tube; the *picrate*, *styphnate*, *picrolonate*, m. p. 160° (decomp.), and very hygroscopic *dihydrochloride*, m. p. 171—172°, were examined. A solution of the ketone in hydrobromic acid (40%) is converted by bromine vapour at 50° into the *dihydrobromide* of *γ-quinolyl δ-methylbromoaminobutyl ketone*, m. p. about 149°, which is transformed by an excess of ice-cold potassium hydroxide solution into *γ-quinolyl 2-N-methylpyrrolidyl ketone*, a pale red, viscous, very unstable liquid which was not further purified; when immediately treated with the calculated amount of very dilute hydrochloric acid it yields a mixture of the *hydrochloride*, $C_{15}H_{16}ON_2,H_2O,HCl$, m. p. 185—186° (decomp.), and a *hydrochloride*, decomp. about 300°, from which the corresponding *base*, m. p. 215° (decomp.), was isolated; the constitution of the latter substances has not been elucidated. Similarly, ethyl quinoline-4-carboxylate and N-ethyl-2-piperidone give the non-crystalline *4-quinolyl 3-N-ethyl-2-piperidonyl ketone*, which was characterised as the *picrate*, decomp. 223—225°. It is slowly hydrolysed to the likewise non-crystalline *4-quinolyl δ-ethylaminobutyl ketone*, the *dihydrochloride*, colourless, hygroscopic powder, decomp. 166—167°, and *dipicrolonate*, pale yellowish-brown precipitate, m. p. 165° (decomp.), of which were examined. Bromination converts the ketone into *4-quinolyl δ-ethylbromoaminobutyl ketone dihydrobromide*, m. p. 161—162° (decomp.).

Ethyl quinate and N-methyl-2-piperidone give *6-methoxy-4-quinolyl 3-N-methyl-2-piperidonyl ketone*, colourless, transparent prisms, m. p. 125—126° (the *hydrochloride* and *picrate*, yellow needles, m. p. 212—213°, are described), which yields *4-methyl-6-quinolyl δ-methylaminobutyl ketone*, viscous liquid (*dipicrolonate*, yellow, crystalline powder, decomp. 212—214°; *dihydrochloride*, canary-yellow needles, m. p. 167—168°), and *4-methoxy-6-quinolyl δ-methylbromoaminobutyl ketone dihydrobromide*, m. p. 134—135°.

Ethyl quinoline-4-carboxylate and *cyclo*hexanone*iso*oxime give a product which can be separated by means of ether into soluble and insoluble *portions*; the former gives a *picrolonate*, m. p. about 130° (decomp.), and appears to be the substance expected, whilst the latter yields a *picrolonate*, m. p. 190°. The crude product is hydrolysed to *4-quinolyl ε-aminoamyl ketone*, dark brown, viscous liquid [*dipicrolonate*, yellow powder, m. p. 206—207° (decomp.); *dihydrochloride*, m. p. about 206° (decomp.)]. Since the lactam of ε-aminohexoic acid under the conditions of the condensation can yield a sodium compound which is transformed by methyl sulphate into the N-methyl ether, the course of the above reaction

could not be regarded as definitely proved. The mode of condensation, however, is deduced from the observation that ethyl-quinoline-4-carboxylate condenses with ε-benzoylaminohexoic lactam in a precisely similar manner, giving a product which is hydrolysed to 4-quinolyl ε-aminoamyl ketone.

Ethyl quinoline-4-carboxylate and ε-methylaminohexoic lactam yield the substance $C_9H_6N{\cdot}CO{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\ CO{\cdot}NMe{\cdot}CH_2\end{matrix}$, m. p. 151—152°, which is hydrolysed to 4-*quinolyl* ε-*methylaminoamyl ketone*, brown, viscous liquid; the *dipicrolonate* is a yellowish-brown powder, m. p. about 195° (decomp.), whereas the *distyphnate* has m. p. 198° (decomp.), and the *dihydrochloride*, m. p. 179—180° (decomp.).

Ethyl 6-methoxypyridine-3-carboxylate, prisms, m. p. 71°, b. p. 135°/0·25 mm., is conveniently prepared by the gradual addition of ethyl coumalate dissolved in alcohol to an alcoholic solution of methylamine. H. W.

Preparation of Derivatives of Hydrastinine. KARL W. ROSENMUND (D.R.-P. 336153; from *Chem. Zentr.*, 1921, iv, 127—128. Compare A., 1920, i, 680).—Instead of alkylideneamines, from formaldehyde and piperonyl*iso*propylamine (see A., 1920, i, 680), compounds of the general formula

$$CH_2<\begin{matrix}O\\ O\end{matrix}>C_6H_3{\cdot}CH_2{\cdot}CHR{\cdot}NR'{\cdot}CH_2{\cdot}OH$$

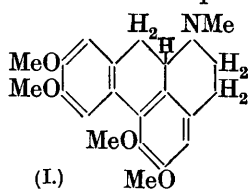
(R = hydrogen or methyl, R′ = hydrogen or alkyl) are treated with catalysts. *Piperonyl*iso*propylaminomethanol* prepared from the base and chloromethyl alcohol, a colourless syrup, is heated with 10% hydrochloric acid for half an hour at 100°, whereby 3-*methyldihydronorhydrastinine* is obtained. The *hydrochloride* has m. p. 232°; the *hydriodide* has m. p. 217°. *Homopiperonylmethylaminomethanol*, $CH_2<\begin{matrix}O\\ O\end{matrix}>C_6H_3{\cdot}[CH_2]_2{\cdot}NMe{\cdot}CH_2{\cdot}OH$, obtained from the base and chloromethyl alcohol, is a syrup which gives on heating with 10% sulphuric acid *dihydrohydrastinine*. From *homopiperonylethylaminomethanol*, a colourless, unstable syrup, by heating with 12% hydrochloric acid, N-*ethyldihydronorhydrastinine hydrochloride* is obtained in white needles. By the action of chloromethyl alcohol on the secondary base, *piperonyl*iso*propylmethylaminomethanol* is obtained, a colourless syrup, resinifying on warming, which gives on heating with hydrochloric acid 3-methyldihydrohydrastinine hydrochloride; needles, m. p. 230—232°. G. W. R.

Laurotetanine, the Tetanising Alkaloid of Various *Lauraceæ*. K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1921, [iii], **3**, 180—198. Compare Greshoff, A., 1891, 334. Filippo, A., 1899, i, 312.)—The author prepared laurotetanine in a yield of 0·38%, from the bark of *Litsea cubeba*, Pers.; it probably occurs in some dozen other *Lauraceæ*. $[\alpha]_D^{25}$ +98·5°. The moist alkaloid crystallised from acetone, has m. p. 125° (not 134° as indicated by Filippo). It has the composition $C_{19}H_{23}O_5N$ (Filippo), but loses $\frac{1}{2}H_2O$ in a vacuum over sulphuric acid, and a second $\frac{1}{2}H_2O$ at 80° over phosphoric

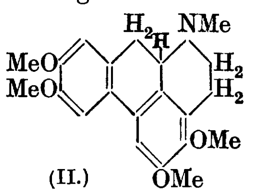
oxide, so that the anhydrous alkaloid is $C_{19}H_{21}O_4N$. It is a phenolic base, readily oxidises, and is coloured yellow, but withstands electrolytic reduction. The composition of laurotetaninephenylthiocarbamide, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_{19}H_{20}O_4N$, m. p. 211—212°, confirms the anhydrous formula. Laurotetanine hydrobromide, $C_{19}H_{21}O_4N,HBr$, crystallises with 6, the hydriodide with $5H_2O$. The sulphate, B_2,H_2SO_4, with 12 and $5H_2O$, the picrate, m. p. 148°, with $1\frac{1}{2}H_2O$.

Dibenzoyllaurotetanine melts at 169—170°; Filippo's compound was probably the mono-*N*-benzoyl derivative. Nascent diazomethane (from nitrosodimethylurethane) methylates only the single hydroxyl group, forming *laurotetanine methyl ether*, amorphous, insoluble in sodium hydroxide, and yielding a crystalline *sulphate, hydrochloride*, $C_{20}H_{23}O_4N,HCl,1\frac{1}{2}H_2O$, m. p. 245°, *oxalate*, $B_2,C_2H_2O_4$, m. p. 233°, and *thiocarbamide*, m. p. 154—155°.

On the other hand, preformed diazomethane in ethereal solution furnishes N-*methyllaurotetanine methyl ether* (iso*glaucine*), $C_{21}H_{25}O_4N,3H_2O$, m. p. 63°, $[\alpha]_D^{27°}+109°$; this base sublimes unchanged in a vacuum. It is isomeric with glaucine (compare A., 1912, i, 48), which it resembles closely in optical rotation, colour reactions, and pharmacological properties. *iso*Glaucine, *hydrochloride*, crystallises with 2 and with $5H_2O$ and melts when anhydrous at 239°, the *hydrobromide* at 252°; the l-*hydrogen tartrate*, $C_{21}H_{25}O_4N,C_4H_6O_6,3H_2O$, loses $2H_2O$ in a vacuum over phosphoric oxide at 80°, the rest at 110°. The *methiodide* melts at 229°. These salts differ from the corresponding salts of glaucine.



(I.)

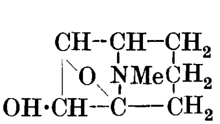


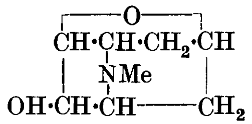
(II.)

According to the author, the difference between glaucine (I) and *iso*glaucine (II) must lie in the orientation of the methoxy-groups. Formula I was established synthetically by Gadamer, who states that the colour reactions are due to unsubstituted 1 : 4-positions in the ring on the extreme left of the above formula. As these reactions are shared by *iso*glaucine, the author concludes that the difference is in the lowest ring. By oxidation of laurotetanine with alkaline permanganate, he has obtained 1 : 2-methoxybenzene-3 : 4 : 5-tricarboxylic acid, which must be derived from the lowest ring, since this is the only one attached to three carbon atoms. At the same time, it follows that the two methoxy-groups of this ring are equally in ortho-positions in *iso*glaucine, so that the only way in which (on the above suppositions) a difference from glaucine can be expressed is by formula II. G. B.

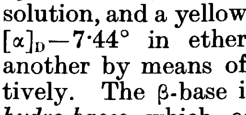
Scopoline. J. Gadamer and Fritz Hammer (*Arch. Pharm.*, 1921, **259**, 110—135).—An extended study of the behaviour of inactive scopoline in Hofmann's degradation process has led Hess

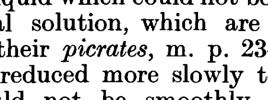
(A., 1918, i, 404; 1920, i, 81) to put forward the annexed formula (I), for the alkaloid. This is adversely criticised, since it involves the assumption that an oxygen bridge formed under considerable strain is highly stable and also does not explain the formation of the number of ψ-demethylscopolines and tetrahydro-ψ-demethylscopolines actually isolated. Hofmann's process has therefore now been applied to the optically active scopolines (compare King, T., 1919, **115**, 496), and the results obtained are considered to be in harmony with formula II.


(I.)

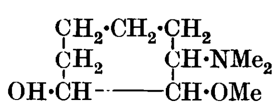

(II.)

d-Scopoline is converted by methyl iodide into the corresponding *methiodide*, long needles, which remain unchanged below 270°, $[\alpha]_D + 31{\cdot}7°$ in aqueous solution. The latter is transformed by silver oxide into the ammonium *base*, which, when distilled under diminished pressure, gives the stable *d-α-ψ-demethylscopoline*, m. p. 44—45°, $[\alpha]_D - 30{\cdot}2°$ in alcoholic solution, and unstable d-β-*ψ-demethylscopoline*, a colourless, viscous liquid, b. p. 88—89°/1 mm., $\alpha_D - 18° \ 30'$ in 0·2-dcm. tube (formulæ III and IV). The α-base is reduced by hydrogen in the presence of palladianised charcoal to a mixture of the corresponding *tetrahydro-α-bases*, small needles, m. p. 73—74°, $[\alpha]_D + 25{\cdot}7°$ in ethereal solution, and a yellow liquid which could not be caused to crystallise, $[\alpha]_D - 7{\cdot}44°$ in ethereal solution, which are separated from one another by means of their *picrates*, m. p. 234° and 144° respectively. The β-base is reduced more slowly to a mixture of *tetrahydro-bases* which could not be smoothly separated from one another by means of their *picrates* (m. p. 162 and 118° respectively) or picrolonates. From the latter picrate, however, it was found possible to isolate one of the *d*-tetrahydro-ψ-demethylscopolines, m. p. 98°, $[\alpha]_D - 19{\cdot}0°$ in ethereal solution.


(III.)

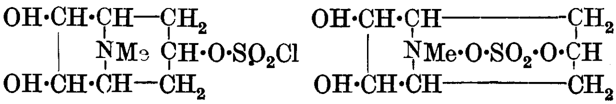

(IV.)

The behaviour of the α-tetrahydro-ψ-demethyl-*d*-scopoline bases when subjected to Hofmann's degradation process is described. The base from the picrate, m. p. 234°, yields a *methiodide*, long, pointed needles, m. p. 264°, $[\alpha]_D + 4{\cdot}9°$ in aqueous solution, which is converted successively into the oily *ammonium* base and *O-methyltetrahydro-ψ-demethyl*-d-*scopoline* (annexed formula), $[\alpha]_D - 3{\cdot}9°$ in ethereal solution (*picrate*, m. p. 138°). Similarly, the base from the picrate, m. p. 144°, yields successively a *methiodide*, needles, m. p. 204°, the optical activity of which could not be demonstrated, a syrupy ammonium base, and an O-*methyl* compound, $[\alpha]_D - 15{\cdot}9°$ in ethereal solution.



l-Scopoline is converted by a solution of hydrogen bromide in glacial acetic acid at 125—127° into a mixture of *l*-scopoline hydrobromide, inactive hydroscopoline bromide hydrobromide, small prisms, m. p. 202°, and a *substance*, needles, m. p. 96—97°, $[\alpha]_D$ $-12{\cdot}56°$ in aqueous solution. The formation of the second, optically inactive substance is considered to be particularly significant, since, according to Hess's formula, the asymmetry of the molecule would not be destroyed by the rupture of the oxygen bridge and thus an optically active compound would be expected; this is not the case with the authors' formula. Reduction of the bromohydrobromide from the *l*-base by hydrogen in the presence of palladianised charcoal leads to the production of optically inactive hydroscopoline hydrobromide, m. p. 218° (decomp.).

l-Scopoline reacts with cold chlorosulphonic acid, addition occurring primarily at the ethereal oxygen atom and being followed by conversion into the *substance* (V) which when brought into contact with ice gives the inner *salt* (VI). The latter substance has



(V.) (VI.)

not been characterised definitely, since it is contaminated with the disulphate formed owing to the simultaneous esterification of the hydroxyl group attached to carbon atom 1. When hydrolysed by hydrochloric acid, it is converted into *hydroxyhydroscopoline*, which was isolated in the form of its *hydrochloride*, slender, hygroscopic needles, m. p. above 285°, $[\alpha]_D$ $-13{\cdot}5°$ in aqueous solution, and *aurichloride* ($+H_2O$), small leaflets, m. p. 214°. Hydroxyhydroscopoline may therefore be regarded as an isomeride of teloidine from which, however, it differs in being optically active (compare King, T., 1919, **115**, 487).

It is suggested that the scopoline residue does not exist as such in scopolamine, but is only formed on fission of the latter. Examination of the action of hydrogen bromide and glacial acetic acid did not, unfortunately, throw any light on this point, since the products isolated were identical with those obtained from scopoline.

H. W.

The Alkylation of Theobromine. Heinrich Biltz and Fritz Max (*Annalen*, 1921, **423**, 318—323. Compare this vol., i, 606—618).—The work of Strecker (*Annalen*, 1861, **118**, 170) and of van der Slooten (A., 1897, i, 382) on the formation of caffeine, 1-ethyltheobromine, and 1-*n*-propyltheobromine by the action of methyl, ethyl, and *n*-propyl iodides on the silver salt of theobromine has been repeated and their results have been confirmed. 1-n-*Butyltheobromine*, prepared similarly, separates from water in silky needles, m. p. 119° (corr.).

When 1-*n*-propyltheobromine is chlorinated in the presence of methyl alcohol at 0°, oxidation takes place in position 8 as well as in positions 4 and 5, and the product is 4 : 5-*dimethoxy*-1-n-*propyl*-

3 : 7-*dimethyl*-4 : 5-*dihydrouric acid*, which crystallises from water, often in rhombic, more frequently in hexagonal tablets, sinters at 140°, m. p. 148° (corr., decomp.). On reduction by means of stannous chloride and hydrochloric acid, it yields 1-n-*propyl*-3 : 7-*dimethyluric acid*, silky needles, m. p. 293° (corr., decomp.), solubility in boiling water about 0·8.

4 : 5-*Dimethoxy*-1-n-*butyl*-3 : 7-*dimethyl*-4 : 5-*dihydrouric acid*, short prisms, sinters at 150°, m. p. 154° (corr.), and 1-*n*-butyl-3 : 7-dimethyluric acid, needles, m. p. 270° (corr.), may be prepared in a similar manner from 1-*n*-butyltheobromine. C. K. I.

Formyl Derivatives of Secondary Bases. E. MERCK (D.R.-P. 334555; from *Chem. Zentr.*, 1921, ii, 1020).—Formyl derivatives of secondary bases are obtained by the action of chloral hydrate on the free bases. By the action of chloral hydrate on 2-methylhomopiperonylmethylamine, with cooling, a *formyl* compound is obtained crystallising from chloroform in long, lustrous needles, m. p. 94—95°. From piperidine, *formylpiperidine* is obtained, as an oil, b. p. 106—110°/17 mm. G. W. R.

Derivatives of δ- and ε-Amino-acids. L. RUZICKA (*Helv. Chim. Acta*, 1921, **4**, 472—482).—Simplified methods are described which are suitable for the production of δ-methylaminovaleric and ε-methylaminohexoic acids in quantity.

N-Methylpiperid-2-one, a colourless, mobile oil, b. p. 104°/14 mm. (compare Fischer and Bergmann, A., 1913, i, 710), is obtained in quantitative yield by the reduction of 1-methyl-2-pyridone by hydrogen in aqueous solution in the presence of platinum black and is hydrolysed by boiling concentrated hydrochloric acid to δ-methylaminovaleric acid, colourless needles, m. p. 126—127° (Fischer and Bergmann give m. p. 121°). Similarly, 1-ethyl-2-pyridone is reduced by sodium and alcohol to the *substance*, $C_{14}H_{26}N_2$, a colourless, viscous liquid, b. p. 120—125°/12 mm., but by hydrogen and platinum black to 1-*ethyl*-2-*piperidone*, a colourless liquid, b. p. 107—108°/12 mm. The latter yields δ-*ethylaminovaleric acid*, coarse prisms, m. p. 138—139°, from which the corresponding *benzoyl* derivative, m. p. 97—98° and *ethyl* δ-*benzoylethylaminovalerate*, a colourless, viscous liquid, b. p. 165°/0·5 mm., are obtained.

[With C. T. SEIDEL and E. HUGOSON]. The *lactam* of ε-aminohexoic acid, $CH_2{<}{\begin{matrix}CH_2{\cdot}CH_2{\cdot}NH\\ CH_2{\cdot}CH_2{\cdot}CO\end{matrix}}$, b. p. about 140°/12 mm., is obtained in 66% yield by a modification of Wallach's process (A., 1900, i, 590), and is converted into the corresponding *benzoyl* derivative, b. p. 150—155°/vacuum, m. p. 45—47°. The former is hydrolysed by concentrated hydrochloric acid to ε-aminohexoic acid, which, when esterified, yields *ethyl* ε-*aminohexoate*, a colourless mobile oil, b. p. 80—82°/1 mm., 60—62°/0·05 mm.; the ester can also be prepared from ε-aminohexoic acid hydrochloride. *Ethyl* ε-*benzoylaminohexoate*, b. p. 184—186°/0·1 mm., m. p. 35°, is prepared by the following series of operations: benzoylpiperidine is

transformed by phosphorus pentachloride into α-chloro-ϵ-benzoylaminopentane, which is converted by potassium cyanide into ϵ-benzoylaminohexonitrile which is then directly treated with alcoholic hydrogen chloride.

The lactam cannot be smoothly methylated by formaldehyde, but is converted by the successive action of sodium and methyl sulphate at the atmospheric temperature into the *lactam* of ϵ-methylaminohexoic acid, a colourless, mobile liquid, b. p. 104—106°/11 mm., 120°/25 mm. It is converted by boiling concentrated hydrochloric acid into ϵ-methylaminohexoic acid, m. p. 130—131°. *Ethyl ϵ-benzoylmethylaminohexoate* is a viscous, colourless liquid, b. p. about 170°/vacuum; it is scarcely affected by sodium and methyl sulphate in boiling xylene solution. H. W.

Formyl and Aldehydic Derivatives of Pyrroles and Indoles. L. ALESSANDRI and M. PASSERINI (*Gazzetta*, 1921, **51**, i, 262—285).—The matter contained in this paper and not given in the abbreviated account previously published (A., 1915, i, 988) is as follows.

1-Formyl-2-methylindole, m. p. 76·5°, obtained by the action of *iso*amyl formate on 2-methylindole, yields 2-methylindole when hydrolysed by means of sodium hydroxide solution, and is converted into 2-methylindole-3-aldehyde when heated in a sealed tube with a trace of zinc chloride at 200—210°. 1-Formyl-2 : 5-dimethylpyrrole, m. p. 35°, reduces ammoniacal silver nitrate solution only in the hot, distils virtually unchanged, and yields 2 : 5-dimethylpyrrole-3-aldehyde when heated in a sealed tube at 200—210°.

The compound, m. p. 96°, obtained by methylation of 2 : 5-dimethylpyrrole-3-aldehyde, forms stout, lustrous, pale yellow crystals and consists of 1 : 2 : 5-trimethylpyrrole-3-aldehyde.

2 : 4-Dimethylpyrrole-5-aldehyde, m. p. 89°, forms an *azine*, crystallising in lustrous, yellow needles, m. p. 242° (browning), and an unstable *phenylhydrazone*, crystallising in rosettes of yellow needles, m. p. 74° (decomp.). When methylated, it yields 1 : 2 : 4-trimethylpyrrole-5-aldehyde, which forms an amber-yellow oil, b. p. 130—135°/15 mm., gives no coloration with Schiff's reagent, does not reduce ammoniacal silver nitrate solution, and forms an oxime crystallising in colourless, fibrous prisms, m. p. 145°.

In preparing pyrrole-2-aldehyde from magnesium pyrryl iodide (compare A., 1915, i, 452), the latter is conveniently treated with ethyl in place of *iso*amyl formate. T. H. P.

Molecular Organic Compounds. VI. Additive Compounds of *s*-Trinitroanisole and Trinitro-*m*-cresol Methyl Ether with certain Tertiary Bases. MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1921, **51**, i, 313—317. Compare this vol., i, 193).—The formation of stable, crystalline additive compounds of *s*-trinitroanisole with organic bases such as pyridine, α-picoline, quinoline, and *iso*quinoline may be regarded as comparable with the formation of the picrates of these bases, but the presence in

the trinitroanisole molecule of a labile methoxy-group renders such comparison questionable.

For the compound formed by *s*-trinitroanisole and pyridine, four formulæ are possible, and between these it is not possible to decide. When heated on a water-bath with an alcoholic solution of ammonia or aniline, this compound undergoes no change, but with phenylhydrazine, a reaction apparently takes place; pyridine picrate is readily decomposed by phenylhydrazine under these conditions, phenylhydrazine picrate being formed. The trinitroanisole–pyridine compound is decomposed by boiling aqueous potassium hydroxide, potassium picrate, methyl alcohol, and pyridine being formed. Trinitro-*m*-tolyl methyl ether also contains a labile methoxy-group and unites with pyridine and quinoline, forming stable additive compounds.

The s-*trinitroanisole–pyridine* compound, $OMe{\cdot}C_6H_2(NO_2)_3,C_5H_5N$, forms flattened, golden-yellow prisms, m. p. 114—115°; the s-*trinitroanisole–2-methylpyridine* compound, $OMe{\cdot}C_6H_2(NO_2)_3,C_5H_4NMe$, large, lustrous, greenish-yellow plates, m. p. 138—139°; the s-*trinitroanisole–quinoline* compound, $C_7H_5O_7N_3,C_9H_7N$, lustrous, yellow needles, m. p. 156—157°; the s-*trinitroanisole*–iso*quinoline* compound, lustrous, pale yellow needles, m. p. 161—162°; the *trinitro*-m-*tolyl methyl ether–pyridine* compound, $C_8H_7O_7N_3,C_5H_5N$, long, canary-yellow needles, m. p. 137—138°; and the *trinitro*-m-*tolyl methyl ether–quinoline* compound, $C_8H_7O_7N_3,C_9H_7N$, lustrous prisms, m. p. 183°. T. H. P.

Synthesis of 4-Alkylpyridines. ERNST KOENIGS and WALTER JAESCHKE (*Ber.*, 1921, **54**, [*B*], 1351—1357).—Ethyl 4-chloropyridine-2 : 6-dicarboxylate contains a sufficiently mobile halogen atom to allow a smooth reaction with ethyl sodiomalonate and its derivatives with the formation of substances which readily yield 4-alkylpyridines.

4-Hydroxypyridine-2 : 6-dicarboxylic acid is conveniently converted by successive treatment with phosphorus pentachloride and ethyl alcohol into *ethyl* 4-*chloropyridine*-2 : 6-*dicarboxylate*, long, colourless needles, m. p. 92—94° (corr.), which condenses with ethyl sodiomalonate in the presence of toluene to form *ethyl* 2 : 6-*dicarboxypyridine*-4-*malonate*, $C_5NH_2(CO_2Et)_2{\cdot}CH(CO_2Et)_2$, long, slender needles, m. p. 70—72° (corr.). The latter is hydrolysed by hydrochloric acid (12%) at 110° to 4-methylpyridine-2 : 6-dicarboxylic acid, colourless needles ($+H_2O$), decomp. 245° (corr.), and is transformed at 230—240° into γ-picoline, b. p. 141—143°, which is further identified by conversion into the aurichloride, m. p. 205° (corr.) after softening at 185°.

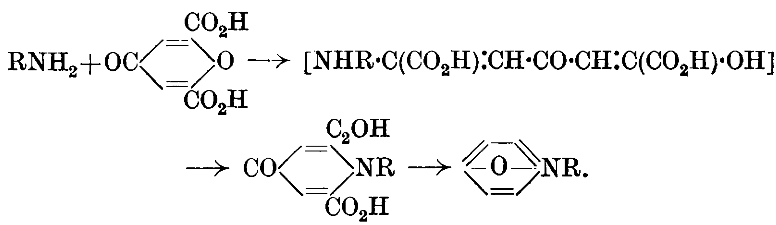
In a similar manner, ethyl 4-chloropyridine-2 : 6-dicarboxylate is condensed with ethyl sodioethylmalonate, and the product is hydrolysed with boiling hydrochloric acid, yielding thereby a mixture of propylpyridine-tetra-, -tri-, and -di-carboxylic acids which was transformed without further purification into 4-*propylpyridine*, a very pale yellow liquid, b. p. 184—186°, d^{15} 0·9381. The new base yields a *hydrochloride*, m. p. 215° (corr.), an *auri-*

chloride, yellow, crystalline precipitate, m. p. 113—115° (corr.), a *platinichloride*, m. p. 204° (corr.), and a *picrate*, slender needles, m. p. 153° (corr.). H. W.

4-Pyridyl Mercaptan and Pyridine-4-sulphonic Acid. Ernst Koenigs and Georg Kinne (*Ber.*, 1921, **54**, [*B*], 1357—1362).—The authors have endeavoured to make use of the comparative mobility of the halogen atom of ethyl 4-chloropyridine-2 : 6-dicarboxylate in the preparation of thiol derivatives of pyridine, but the results were not completely satisfactory, and it was found preferable to use 4-chloropyridine as initial material, although the reaction in this case proceeds much more slowly than with the ester.

Ethyl 4-chloropyridine-2 : 6-dicarboxylate and potassium hydrogen sulphide react in aqueous alcoholic solution at the temperature of the water-bath to give a small yield of *ethyl* 4-*thiolpyridine*-2 : 6-*dicarboxylate*, slender, silky needles, m. p. 176° (corr.). The corresponding *acid* crystallises in slender, colourless needles, m. p. 243° (corr.) [the *lead* salt, $(C_7H_2O_4NS)_2Pb_3$, yellow crystals, is described], and, when distilled, gives 4-*thiolpyridine* in 10—15% yield. This substance is more conveniently prepared by heating 4-chloropyridine (from 4-hydroxypyridine and phosphorus pentachloride at the temperature of boiling water) with potassium hydrogen sulphide in aqueous alcoholic solution at 140°; it crystallises in pale yellow needles, m. p. 177° (corr., decomp.). The *gold* salt, $(C_5H_4NS,HAuCl_4)_3Au$, m. p. 210° (corr.), and *platinum* salt $[(C_5NH_4S)_2,H_2PtCl_6]_2Pt$, m. p. above 335°, are described. The mercaptan is oxidised by iodine to the corresponding *disulphide*, long, colourless needles, m. p. 155° (corr.), which gives an *aurichloride*, m. p. 201° (corr.), and *platinichloride*, golden-yellow needles darkening without melting at about 275°. *Pyridine*-4-*sulphonic acid*, colourless needles, m. p. 134—135° (corr.), is prepared by oxidation of the thiol with nitric acid; the *barium* and *silver* salts are described. H. W.

The Constitution of *N*-Aryl Derivatives of 4-Pyridone. Alexander P. Smirnoff (*Helv. Chim. Acta*, 1921, **4**, 599—612).—A number of N-aryl-4-pyridones have been synthesised from chelidonic acid and arylamines according to the general scheme:



Reaction occurs in at least three distinct stages, including the primary formation of the salt, the opening of the chelidonic acid ring with the formation of the very unstable additive product,

followed by loss of water with the formation of the cyclic dicarboxylic acid which in certain cases could be isolated, and finally evolution of carbon dioxide. The above formula is adopted for the N-aryl-4-pyridones (similar to that of the corresponding alkyl derivatives) as it best harmonises with the complete absence of ketonic properties and the apparently saturated condition of the nitrogen atom.

1-Phenyl-4-pyridone, needles ($+2H_2O$), m. p. 105°, anhydrous, m. p. 125°, is prepared by heating chelidonic acid with an excess of aniline at 120—180°. It gives a *chloride* ($+1H_2O$) which, when dehydrated, does not melt below 330°, an *aurichloride*, golden-yellow needles, m. p. 188°, and a *platinichloride*, pale orange-yellow leaflets, m. p. 208° (decomp.), after softening at 202°. 1-o-*Tolyl*-4-*pyridone* crystallises in colourless, rhombic plates, m. p. 148° [*chloride*, thin prisms ($+H_2O$), m. p. 131° after softening at 123°; the *aurichloride* and *platinichloride* are resinous]. 1-m-*Tolyl*-4-*pyridone* forms colourless plates, m. p. 133—134°, and yields a *chloride* ($+3H_2O$), m. p. 92—93°, an *aurichloride*, small, yellow needles, m. p. 122—123°, and a *platinichloride*, slender, pale-orange needles, m. p. 205° (decomp.). The condensation of chelidonic acid with *p*-toluidine is of particular interest, since in this case the intermediate formation of 4-*keto*-1-p-*tolyl*-1 : 4-*dihydropyridine*-2 : 6-*dicarboxylic acid*, coarse, yellow prisms, m. p. 185° (decomp.) [*phenylhydrazone*, brown leaflets, m. p. about 175° (decomp.), after softening at 160°], could be established. The acid passes by loss of carbon dioxide at 175—185° into p-*tolyl*-4-*pyridone*, m. p. (anhydrous) 142—143°, *dihydrate*, m. p. 78°, which gives a *chloride* ($+3H_2O$), m. p. (anhydrous) 208° (decomp.), an *aurichloride*, golden-yellow leaflets, m. p. 178°, and a *platinichloride*, m. p. 205° (decomp.). 1-*op-Dimethylphenyl*-4-*pyridone* crystallises in colourless prisms ($+H_2O$), m. p. 90°; the corresponding *chloride* is hygroscopic and non-crystalline, whilst the *auri-* and *platini-chlorides* are resinous. 1-α-*Naphthyl*-4-*pyridone* forms colourless platelets, m. p. 173°.

H. W.

Partial Synthesis of Homocincholeupone and certain *cyclo*-Pentanetrione Derivatives. Ernst Koenigs and Walter Ottmann (*Ber.*, 1921, **54**, [*B*], 1343—1350).—The recent publications of Rabe and Kindler (A., 1918, i, 303; 1919, i, 34) have induced the authors to publish an account of the synthesis of optically inactive homocincholeupone; it has not been found possible to accumulate sufficient material to permit the isolation of the active forms and the direct comparison of the natural and synthetic products. An account is also given of several substances which have been isolated during unsuccessful attempts to prepare β-collidine.

Chloralcollidine [3-*ethyl*-4-β-*hydroxy*-γγγ-*trichloro*-n-*propylpyridine*] is prepared by the action of chloral on β-collidine in the presence of zinc chloride; it crystallises in colourless, hexagonal plates, m. p. 137° (corr.), and yields a *hydrochloride*, rhombic plates, m. p. 105° (corr.), and an *aurichloride*, yellow leaflets or plates,

m. p. 173° (corr.). It is converted by alcoholic potassium hydroxide solution into β-3-*ethyl*-4-*pyridylacrylic acid*,

$$N{<}{\begin{matrix}CH{=}CH\\CH{\cdot}CEt\end{matrix}}{>}C{\cdot}CH{:}CH{\cdot}CO_2H,$$

colourless, slender needles, m. p. 247° (corr.), which gives a *hydrochloride*, needles, m. p. 176° (corr.), an *aurichloride*, yellow prisms, m. p. 202° (corr.), and a *dibromo*-derivative, colourless, crystalline powder, m. p. 148° (corr.). The unsaturated acid is reduced by sodium and hot amyl alcohol to *homocincholeupone*, needles, m. p. 225° (corr.); the corresponding *hydrochloride* could not be caused to crystallise, whereas the *aurichloride* forms yellow leaflets, m. p. 178° (corr.). The ethyl ester *hydrochloride* could not be isolated in the crystalline state, whereas the yellow, crystalline *aurichloride* has m. p. 123° (corr.).

Ethyl 3-*ethyl*cyclo*pentane*-1 : 2 : 4-*trioneglyoxylate*,

$$\begin{matrix}CHEt{\cdot}CO\\|\quad\quad\\CO{-}{-}CO\end{matrix}{>}CH{\cdot}CO_2Et,$$

coarse, yellow prisms, m. p. 120—121° (corr.), is formed by the condensation of methyl *n*-propyl ketone with ethyl oxalate in the presence of alcoholic sodium ethoxide solution. The corresponding *acid* crystallises in small, yellow needles, m. p. 185° (corr.); it is converted by boiling concentrated hydrochloric acid into 3-ethyl-cyclo*pentane*-1 : 2 : 4-*trione*, colourless, slender needles ($+2H_2O$), m. p. 96° (corr.), or anhydrous, m. p. 173° (corr., decomp.) after softening at about 68°. The corresponding *monoxime* crystallises in slender needles, m. p. 140° (corr.). H. W.

Preparation of *N*-Substituted Oxindoles. ROBERT STOLLÉ (D.R.-P. 335763; from *Chem. Zentr.*, 1921, ii, 1065—1066).—N-Monohalogen acetyl derivatives of secondary alkylaryl- or diaryl-amines of the general formula $NRR'{\cdot}CO{\cdot}CH_2X$ (R=alkyl or aryl, R'= aryl, X=halogen), are heated with aluminium haloids. Ring formation, whereby the N-oxindole derivative is formed, takes place with elimination of the corresponding hydrogen haloid, the halogen atom of the acetyl group combining with the neighbouring ortho-hydrogen atom of the benzene nucleus. 1-*Ethyl oxindole* is obtained by heating *chloroacetethylanilide* (from chloroacetyl chloride and ethylaniline in presence of alcohol, m. p. about 35°, b. p. 165°/21 mm.) with aluminium chloride for four hours at about 160°; it has m. p. 97° after recrystallising from water or acetone. Chloroacetodiphenylamide, $NPh_2{\cdot}CO{\cdot}CH_2Cl$, when heated with aluminium chloride at 160—170° gives 1-*phenyloxindole*, m. p. 121°. By the action of an oxidising agent such as nitrosodimethylaniline, *diphenyl*iso*indigotin*, m. p. 315°, is obtained. With bleaching powder, 3 : 3-*dichloro*-1-*phenyloxindole* is formed, having m. p. 118°. When *chloroacetomethylanilide* (colourless needles, m. p. 70°) is heated with aluminium chloride at 170—180°, 1-*methyloxindole* is obtained, m. p. 89°. By the action on this of nitrosodimethylaniline or sodium hypoiodite, *dimethyl*iso*indigotin* is obtained, forming dark brown needles, m. p. 265°. Nitrous acid or amyl nitrite and sodium ethoxide give

with 1-methyloxindole, *oximinomethyloxindole*, forming yellow needles. G. W. R.

Actual and Supposed Isomerism in the Isatin Series. A. HANTZSCH (*Ber.*, 1921, **54**, [*B*], 1221—1257).—The author's investigation of isomerism in the isatin series has led to very different and much simpler results than Heller's work (A., 1920, i, 766, and earlier abstracts) and these are in complete harmony with the theories advanced previously on isomerism, tautomerism, and salt formation.

Of the three supposed isomerides of isatin, isatol alone actually exists. The primary product of the methylation of isatin silver is a single crystalline ether, von Baeyer's isatinol methyl ether, $C_6H_4<^{CO}_{-N}>C{\cdot}OMe$. This is converted, for example, by warming its solution in benzene, by isomerisation into the N-methyl ether, $C_6H_4<^{CO-}_{NMe}>CO$; on the other hand, it is extremely readily hydrolysed even by water at the laboratory temperature, but the corresponding compound "isatinol," $C_6H_4<^{CO}_{-N}>C{\cdot}OH$, is never obtained owing to its isomerisation either to isatin or to α- or β-isatol, $C_6H_4<^{C(OH)}_{N}>CO$ and $C_6H_4<^{C(OH)}_{N}>CO$ respectively. Isatin is the main product in aqueous alcoholic solution, isatol being formed by the action of atmospheric moisture on the solid ether; the metastable α-isatol, which can exist only in the solid state, is primarily formed quantitatively, and this is transformed by all solvents into the stable β-isatol. The latter is also mainly formed (in addition to some isatin) by hydrolysis of the isatinol ether in acidified, aqueous-alcoholic solution. Concentrated acid causes the elimination of the methoxy-group with formation of isatin. The free isatols are distinct isomerides and not tautomeric forms, since they do not contain the group $-N{:}C(OH)-$ which can pass directly into the group $-NH{\cdot}CO-$. The substance described by Heller as isatol is not homogeneous, but represents impure β-isatol. Heller's isatinone, which has been regarded successively as an isomeride of isatol and later as methylisatoid, is identical with β-isatol. The other alkylisatoids described by von Baeyer and the many other apparently new isomerides of isatin and 5:7-dimethylisatin obtained by Heller do not exist, and this applies in particular to the apparent lactim or enol form, dimethylisatinol; in this series, also, dimethylisatol is the sole isomeride of dimethylisatin.

[With M. STECHOW.]—Isatinol methyl ether (isatin O-methyl ether), red prisms, m. p. 101—102°, is obtained by the action of methyl iodide on isatin silver in the presence of dry benzene at the ordinary temperature; the success of the method is greatly dependent on the purity of the materials, and it is also necessary to exclude light and moisture. Compact crystals of the ether appear to be stable indefinitely towards air, but the powdered material is rapidly and quantitatively hydrolysed by atmospheric

moisture to α-isatol. The latter is most conveniently prepared by warming isatin silver with methyl iodide on the water-bath for about twenty to thirty minutes; it is a pale yellow powder, m. p. 238—240° (decomp.), which in the solid state can be preserved unchanged indefinitely, but which, even in cold solvents, undergoes immediate isomerisation to β-isatol; it unites with $\frac{1}{2}$HCl to give the red isatol hydrochloride, which, however, gradually loses hydrogen chloride at the ordinary temperature. β-Isatol results when the product from isatin silver and methyl iodide is evaporated to dryness, the residue extracted with ether and benzene to remove isatinol methyl ether, and then crystallised from boiling alcohol; it has m. p. 226°, is indifferent towards diazoacetic acid, but, contrary to Heller's statement, slowly reacts with diazomethane. It combines with concentrated hydrochloric acid, yielding the same red, crystalline hydrochloride, which is prepared from α-isatol. It can also be obtained from isatin silver and ethyl iodide, thus affording further proof of the absence of an alkoxy-group.

Heller has described the preparation of an isatol by the action of benzoyl chloride on isatin silver in the presence of benzene, although the preparations were not invariably successful and the reason of the failures was not fully elucidated. The authors have failed to isolate a homogeneous product by following these directions, and are drawn to the conclusion that Heller's material was impure β-isatol. The product similarly prepared from 5-chloroisatin (Heller's chloroisatol, m. p. 186°) appears to be a mixture of 5-chloroisatin and benzoic acid.

Von Baeyer and Oekonomides's ethylbromoisatoid,

$$C_{18}H_{12}O_4N_2Br_2,$$

is in reality 5-bromoisatol, $C_6H_3Br{<\!\!\!<}{\overset{C(OH)}{\underset{N}{}}}{>}CO$, prismatic crystals, m. p. 247°, since it is formed from 5-bromoisatin silver and either methyl or ethyl iodide; the discrepancies in the analyses are due to the very considerable difficulties involved in the purification of the product.

3-*Dichloroisatin*, $C_6H_4{<}{\overset{CCl_2}{\underset{NH}{}}}{>}CO$, pale yellow, prismatic crystals, m. p. 165° (decomp.), is obtained by the action of phosphorus pentachloride on isatin in the presence of benzene at the atmospheric temperature; its constitution is deduced from its conversion into the known β-phenylhydrazone, m. p. 210°. Similarly, isatin N-methyl ether and isatinol methyl ether (the latter by isomerisation) yield 3-dichloroisatin N-methyl ether, m. p. 143°. Attempts to prepare isatol chloride, $C_6H_4{<\!\!\!<}{\overset{CCl}{\underset{N}{}}}{>}CO$, were not completely satisfactory; the dichloride does not lose hydrogen chloride smoothly when heated alone or in the presence of concentrated sulphuric acid, whilst a uniform product was not obtained from the pentachloride and isatol. H. W.

The Constitution of the Salts derived from Isatin and Analogous Substances. A. HANTZSCH (*Ber.*, 1921, **54**, [*B*], 1257—1267. Compare preceding abstract).—Heller (A., 1917, i, 219)

has described two structurally isomeric silver salts of isatin which he formulates $C_6H_4<\genfrac{}{}{0pt}{}{CO}{-N}\geqslant C\cdot OAg$ and $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{NAg}>CO$ respectively, and has further considered the violet alkali salts of isatin as N-salts, for example, $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{NNa}>CO$, instead of O-salts. Further (A., 1917, i, 220), dioxindole is considered to form primarily the violet salts of the type $C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{NNa—}>CO$, which subsequently undergo transformation into the colourless O-salts, and similar ideas are applied to different complex compounds which contain the group $-CO\cdot CO\cdot NH-$ within a ring. Finally, the dark alkali salts of the 1 : 2-indandiones with the group $-CO\cdot CO\cdot CH\cdot R-$ are regarded as C-salts of the type $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{CRX}>CO$ instead of enolic salts, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CR}\geqslant C\cdot OX$. Since the existence of these types is incompatible with the results previously obtained by Claisen, W. Wislicenus, and Hantzsch, the work has been repeated with the result that the N-salts are shown to be impure products.

Pure isatin silver can be obtained only if all trace of alkalinity in the solution is avoided and preferably by addition of a hot aqueous solution of pure silver acetate to an aqueous alcoholic solution of isatin; isatin silver is precipitated in 75% yield, the remainder being retained dissolved by the liberated acetic acid. The salt is Bordeaux-red and soluble in pyridine with a violet coloration; it readily reacts with pure methyl iodide, yielding primarily the O- and not the N-methyl ether, so that it appears to be a true O-salt. If, however, mixed solutions of silver nitrate and sodium acetate are used (in the preparation of isatin silver), particularly if the latter is present even in slight excess, the precipitate frequently has a brown to black colour, which is not due, however, to the N-salt but to co-precipitation of silver oxide. Increasing amounts of the latter diminish the solubility of the silver salt in pyridine and its rate of reaction with methyl iodide, thus causing isomerisation of the O-methyl to the N-methyl ether. The salts of isatin with the more positive alkali metals are still more certainly O-derivatives and the production of the N-methyl ether from them is due to the fact that they react more slowly than the silver salt with methyl iodide. Optical investigation shows that there are three series of isatin derivatives differing in colour (excluding isatol derivatives): (1) orange-coloured N-derivatives such as free isatin, N-alkyl ethers, N-mercury salts; (2) red to brownish-red O-derivatives such as the O-alkyl ethers and O-pseudo salts (silver salts); and (3) dark violet O-derivatives such as the conjugated or true salts, silver pyridine salts, alkali salts, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{-N}\geqslant C-\underset{\underset{X}{\vdots}}{O}$ or $C_6H_4<\genfrac{}{}{0pt}{}{CO}{N-}>C-\overset{\overset{X}{\vdots}}{O}$, isatin ions.

Heller's violet dioxindole N-salts do not exist; the primary salts of dioxindole are colourless and pass by oxidation into the violet

salts of the primary oxidation product of dioxindole, the so-called isatide. This is shown most distinctly by the behaviour of dioxindole towards freshly-boiled barium hydroxide solutions.

The violet alkali salts of the 1 : 2-indanediones are precisely similar to the salts from the 1 : 3-derivatives, and hence are to be regarded as normal enol salts of the type $-RC{:}C(OX){\cdot}CO-$.

H. W.

Kynurenic Acid. E. BESTHORN (*Ber.*, 1921, **54**, [*B*], 1330—1334).—Kynurenic acid was isolated by Liebig from the urine of the dog and identified with great probability by Homer (A., 1914, i, 730) as 4-hydroxyquinoline-2-carboxylic acid. This view is confirmed by the observation that kynurenic acid and acetic anhydride give a dye very similar to that yielded by other quinoline-2-carboxylic acids and, more explicitly, by a new synthesis of kynurenic acid.

4-Methoxy-2-methylquinoline is condensed with formaldehyde and the product is oxidised by nitric acid to 4-*methoxyquinoline-2-carboxylic acid*, almost colourless needles, m. p. 196—197° (decomp.); the *sodium* and *iron* salts are described. Treatment with boiling hydrobromic acid converts the methoxy-acid into 4-hydroxyquinoline-2-carboxylic acid, m. p. 282—283° (decomp.) after previous softening; the *barium* salt crystallises in slender, microscopic needles. It decomposes at about 300° into carbon dioxide and 4-hydroxyquinoline [kynurene], m. p. 201°. H. W.

Coloured Derivatives of Tetraphenylmethane. III. New Synthesis of Carbazine [Dihydroacridine] Dyes. F. KEHRMANN, M. RAMM, and CH. SCHMAJEWSKI (*Helv. Chim. Acta*, 1921, **4**, 538—546. Compare A., 1919, i, 552).—The synthesis of carbazine dyes has been effected in certain instances according to the scheme

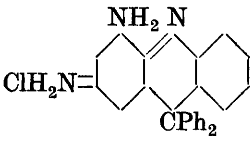
$$C_6H_2Cl(NO_2)_3+H_2N{\cdot}C_6H_4{\cdot}CHR_2 \longrightarrow C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}CHR_2 \longrightarrow$$

$C_6H_2(NO_2)_2{<}^{NH}_{CR_2}{>}C_6H_4$, where R is an aromatic group.

Picryl chloride and *o*-toluidine yield 2 : 4 : 6-*trinitrophenyl*-o-*toluidine*, orange-red prisms, m. p. 164°, whilst with *o*-aminodiphenylmethane and *o*-cumidine the chloride gives the *compounds* $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2Ph$, orange-yellow leaflets, m. p. 140° and $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4Pr^{\beta}$. In no case could ring closure with loss of nitrous acid be effected. *o*-Aminotriphenylmethane and picryl chloride give the expected product, $C_{25}H_{18}O_6N_4$, dark brown, lustrous prisms, m. p. 180°, the *potassium* derivative of which passes in boiling quinoline into 1 : 3-*dinitro*-5 : 5-*diphenyldihydroacridine*, orange-yellow prisms, m. p. 232°. 2 : 6-*Dinitrophenyl*-o′-*benzhydrylphenylamine*, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}CHPh_2$, flattened, yellow needles, m. p. 175°, is convertible under definite conditions into 1-nitrodiphenylcarbazine, whereas 2 : 4-*dinitrophenyl*-o′-*benzhydrylphenylamine*, yellow leaflets, has not been transformed into the corresponding 3-nitro-derivative.

Reduction of 1 : 3-dinitro-5 : 5-diphenyldihydroacridine by stan-

nous chloride and hydrochloric acid in the presence of much alcohol



leads to the isolation of the *tin* double salt of the 1 : 3-diamino-compound which is directly oxidised by concentrated ferric chloride solution to 1-*amino*-5 : 5-*diphenyldihydroacridine*-3-*immonium chloride* (annexed formula), almost black, lustrous needles (the dark chocolate-coloured *platinichloride* and the *perchlorate* dark, brown needles, are also described).

1-Nitrodiphenyldihydroacridine, dark red crystals, m. p. 216—217°, is obtained in poor yield when the product of the condensation of 2-chloro-1 : 3-dinitrobenzene and *o*-aminotriphenylmethane is heated for some time at 200—230°, and is identical with the substance obtained in minor amount by the nitration of diphenyldihydroacridine.

The isolation of the 1 : 3-dinitrodiphenyldihydroacridine throws further light on the structure of the dinitro-compounds previously obtained. The compound, m. p. 322·5°, is without doubt the 3 : 8-derivative, whilst that of m. p. 288° must be the 1 : 8-compound, since all three substances are transformed by further nitration into the same 1 : 3 : 8-trinitro-derivative. It is also rendered probable that the only tetranitro-compound known is the 1 : 3 : 8 : 10-product. H. W.

Influence of Substitution in the Components on the Equilibria in Binary Solutions. XXVIII. The Binary System of 2 : 4-Dinitrophenol with the Three Isomeric Phenylenediamines. ROBERT KREMANN and OTHMAR ZAWODSKY (*Monatsh.*, 1921, **41**, 543—553).—*o*-Phenylenediamine and 2 : 4-dinitrophenol give an equimolecular *compound* the eutectic of which with dinitrophenol lies at 85·3° and 74% by weight of the phenol and with *o*-phenylenediamine at 72° and 43% by weight of the phenol. Examination of the system *m*-phenylenediamine–2 : 4-dinitrophenol similarly discloses the existence of an equimolecular *compound*. *p*-Phenylenediamine (1 mol.) gives a *compound* with 2 : 4-dinitrophenol (3 mols.) and probably also with the phenol (2 mols.). H. W.

Nitro-derivatives of Phenazonium. F. KEHRMANN and JWAN EFFRONT (*Helv. Chim. Acta*, 1921, **4**, 517—526).—Nitro-derivatives of phenazonium are readily prepared by the action of ferric chloride or concentrated nitric acid on the nitro-derivatives of alkyl- or aryl-dihydrophenazines, $C_6H_2(NO_2)_2{<}{}^{NH}_{NR}{>}C_6H_4+HNO_3+2HNO_2=C_6H_2(NO_2){\lessdot}{}^{N\text{———}}_{NR(NO_3)}{>}C_6H_4+2H_2O+2NO$. The nitrates and perchlorates are crystalline and vary from lemon-yellow to orange-red in colour. They are, in general, powerful oxidising agents. Certain nitro-derivatives of alkyldihydrophenazines are prepared from picryl chloride and monoalkylated *o*-diamines. The former can in some cases be replaced by 2-chloro-

1 : 3-dinitrobenzene, but ring closure has not been effected with 4-chloro-1 : 3-dinitrobenzene.

2 : 6-*Dinitrophenyl*-o-*phenylenemethyldiamine*,

$$NHMe{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

long, slender, reddish-brown needles, m. p. 168°, is prepared by the interaction of chloro-2 : 6-dinitrobenzene on *o*-phenylenemethyldiamine in alcoholic solution in the presence of sodium acetate. It is rapidly converted in hot alcoholic alkaline solution into 1-*nitro*-5-*methyldihydrophenazine*, dark violet needles, m. p. 140° (*perchlorate* of 1-*nitro*-5-*methylphenazonium*, sandy, crystalline powder). *Phenyl*-2 : 6-*dinitrophenyl*-o-*phenylenediamine*, $NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, could not be obtained in the crystalline state; it is converted by boiling in quinoline solution and subsequent treatment with aqueous ferric chloride into 1-*nitro*-5-*phenyldihydrophenazine*, $NO_2{\cdot}C_6H_3{<}{\genfrac{}{}{0pt}{}{NH}{NPh}}{>}C_6H_4$, violet, crystalline leaflets, m. p. 181°, from which the corresponding *phenazonium perchlorate* is prepared. 1 : 3-Dinitro-5-phenyldihydrophenazine forms dark violet, lustrous crystals, m. p. 239°. 1 : 3-*Dinitro*-5-*methylphenazonium nitrate* and *perchlorate*, 1 : 3-*dinitro*-5-*ethylphenazonium perchlorate*, and 1 : 3-*dinitro*-5-*phenylphenazonium nitrate* and *perchlorate* are also described. 1 : 3 : 7-Trinitro-5-phenyldihydrophenazine forms nearly black crystals; 1 : 3 : 7-*trinitro*-5-*phenylphenazonium perchlorate* crystallises in yellowish-brown needles. 3-*Nitro*-1-*amino*-5-*phenyldihydrophenazine* is obtained by the partial reduction of the corresponding dinitro-compound with sodium sulphide, but is too unstable to permit its isolation in the pure state. It is converted in the usual manner into 3-*nitro*-1-*amino*-5-*phenylphenazonium perchlorate*.

H. W.

Pyrazines. C. Gastaldi (*Gazzetta*, 1921, **51**, i, 233—255).—The author deals with the composition and structure of the so-called bisulphite compounds of the oximinoketones, $R{\cdot}CO{\cdot}CH{:}NOH$ and $R{\cdot}CO{\cdot}CR_1{:}NOH$, their behaviour towards potassium cyanide, and their transformation into derivatives of *p*-diazine.

Pechmann (A., 1888, 146; 1890, 51) prepared the sodium hydrogen sulphite compound of oximinoacetophenone, from which phenylglyoxal is obtained by the action of dilute sulphuric acid, and to which Pinner (A., 1903, i, 123) ascribed the formula $OH{\cdot}CPh(NaSO_3){\cdot}CH(NaSO_3){\cdot}NH{\cdot}NaSO_3$. The author has repeated Pechmann's work and finds that the formulæ given by Pechmann and by Pinner are erroneous and that oximinoacetone and oximinoacetophenone react with two, rather than with three, molecules of sodium hydrogen sulphite. In fact, of the two groups of oximinoketones capable of reacting with sodium hydrogen sulphite, only the group $\cdot CH{:}NOH$, and not the carbonyl group, reacts, being converted into the group $:CH{\cdot}NH{\cdot}SO_3H$; the reaction is thus analogous to the formation of aminosulphonic acid from sulphur dioxide and hydroxylamine.

The *sodium hydrogen sulphite* compound of *oximinoacetone*, $NaSO_3{\cdot}CHAc{\cdot}NH{\cdot}SO_3Na$, forms silky, hydrated prisms, which

effloresce with loss of their water of crystallisation. The compound of *oximinoacetophenone*, $NaSO_3{\cdot}CHBz{\cdot}NH{\cdot}SO_3Na$, shows similar form and behaviour; the formation of Pinner's 2-benzoyl-4-phenylglyoxaline-3-sulphonic acid (A., 1905, i, 476) was not observed.

The reaction between oximino-compounds, in particular oximino-ketones and sodium hydrogen sulphite, is explainable by the following scheme:

$$R{\cdot}CO{\cdot}CH{:}NOH + H_2SO_3 + H_2O \longrightarrow R{\cdot}CO{\cdot}CH(OH)_2 + NH_2{\cdot}SO_3H, \text{ and}$$

$$R{\cdot}CO{\cdot}C\begin{cases} H \\ OH + H & O{\cdot}SO{\cdot}OH \\ OH \quad H & NH{\cdot}SO_2{\cdot}OH \end{cases} \rightarrow R{\cdot}CO{\cdot}CH(O{\cdot}SO{\cdot}OH){\cdot}NH{\cdot}SO_2{\cdot}OH +$$

$2H_2O$. This scheme is in complete agreement with the analytical data obtained by the author, and also explains the hydrolytic scission of the compounds of oximino-acetone and -acetophenone into methyl- and phenyl-glyoxal respectively; such scission yields first the glycol, $R{\cdot}CO{\cdot}CH(OH)_2$, sodium hydrogen sulphite and sodium aminosulphonate, the glycol then undergoing dehydration to the keto-aldehyde and the aminosulphonate hydrolysis to ammonia and sodium hydrogen sulphate.

The sodium hydrogen compound of benzaldoxime should, therefore, have the structure $NaSO_2{\cdot}O{\cdot}CHPh{\cdot}NH{\cdot}SO_3Na$, and not that suggested by Pechmann, namely, $NaSO_3{\cdot}CHPh{\cdot}NH{\cdot}SO_3Na$, and should, with dilute sulphuric acid, give first the glycol, $CHPh(OH)_2$.

Analogous to the scission of these oximinoketone compounds is the behaviour of benzylideneaminosulphonic acid (Krafft and Bourgeois, A., 1892, 700), and in the formation of acetone and aminosulphonic acid by the interaction of acetoneoxime and sulphurous acid (Schmidt, A., 1892, 476) the production of similar intermediate products must be assumed.

The action of potassium cyanide on the aqueous solution of the sodium hydrogen sulphite compound of oximinoacetone (or oximinoacetophenone) yields the potassium salt of the cyano-derivative of aminoacetonesulphonic (or aminoacetophenonesulphonic) acid: $R{\cdot}CO{\cdot}CH(SO_3Na){\cdot}NH{\cdot}SO_3Na + 2KCN \rightarrow R{\cdot}CO{\cdot}CH(CN){\cdot}NH{\cdot}SO_3K + KO{\cdot}SO_2Na + NaCN$. Hydrolysis of the sulphonic acids thus obtained should yield either cyano-ketone and hydroxylamino-sulphonic acid or cyanoamino-ketone, $R{\cdot}CO{\cdot}CH(CN){\cdot}NH_2$, and sulphurous acid. Of these two reactions the second actually takes place, but in place of cyanoamino-ketones, their condensation products, namely, pyrazine derivatives, are obtained. Thus, cyanoacetoneaminosulphonic acid, $CN{\cdot}CHAc{\cdot}NH{\cdot}SO_3H$, yields 3 : 6-dicyano-2 : 5-dimethylpyrazine, and cyanoacetophenoneamino-sulphonic acid, 3 : 6-dicyano-2 : 5-diphenylpyrazine and 3-cyano-2 : 5-diphenylpyrazine. When heated with aqueous or aqueous alcoholic potassium hydroxide, 3 : 6-dicyano-2 : 5-dimethyl (or diphenyl) pyrazine yields, not 2 : 5-dimethyl (or diphenyl) pyrazine-3 : 6-dicarboxylic acid, but 6-hydroxy-2 : 5-dimethyl (or diphenyl) pyrazine-3-carboxylic acid, one of the cyanogen groups undergoing normal hydrolysis and the other replacement by hydroxyl; liberation of hydrocyanic acid is actually observed.

These pyrazinemonocarboxylic acids give salts by replacement of both the hydroxylic and carboxylic hydrogen, and when fused lose carbon dioxide with formation of 6-hydroxy-2 : 5-dimethyl (diphenyl) pyrazine. 3-Cyano-2 : 5-diphenylpyrazine is hydrolysed normally to the carboxylic acid, which gives 2 : 5-diphenylpyrazine (Staedel, A., 1878, 420) when fused.

The structural formulæ of the pyrazine derivatives obtained are confirmed by their reduction by means of hydriodic acid and red phosphorus, the cyanogen groups being replaced by hydrogen atoms to give 2 : 5-diphenylpyrazine, which is subsequently transformed into 2 : 5-diphenyl-3 : 6-dihydropyrazine (Gabriel and Lieck, A., 1908, i, 465); the latter is thus formed from 3-cyano-2 : 5-diphenylpyrazine or 3 : 6-dicyano-2 : 5-diphenylpyrazine, and also results when 6-hydroxy-2 : 5-diphenylpyrazine is reduced by means of hydriodic acid and red phosphorus.

3 : 6-*Dicyano*-2 : 5-*dimethylpyrazine*, $CN\cdot C\genfrac{}{}{0pt}{}{<N:CMe>}{<CMe\cdot N>}C\cdot CN$, forms lustrous, white laminæ, m. p. 207°, sublimes at about 180°, and exhibits normal cryoscopic behaviour in benzene. 6-*Hydroxy*-2 : 5-*dimethylpyrazine*-3-*carboxylic acid*, $OH\cdot C\genfrac{}{}{0pt}{}{<N:CMe>}{<CMe\cdot N>}C\cdot CO_2H$, forms colourless prisms, m. p. 270° (losing carbon dioxide), and in aqueous solution is acid towards litmus and methyl-orange; its *sodium* salt, $C_7H_6O_3N_2Na_2,4H_2O$, was analysed. 6-*Hydroxy*-2 : 5-*dimethylpyrazine*, $C_6H_8ON_2$, crystallises in colourless tufts, m. p. 207°, and sublimes at about 200°.

Potassium cyanoacetophenoneaminosulphonate,

$$CN\cdot CHBz\cdot NH\cdot SO_3K,$$

forms lustrous, white laminæ.

3-*Cyano*-2 : 5-*diphenylpyrazine*, $C_{17}H_{11}N_3$, crystallises in long prisms, m. p. 119—120°, and dissolves in concentrated sulphuric acid with an orange-yellow coloration. 3 : 6-*Dicyano*-2 : 5-*diphenylpyrazine*, $C_{18}H_{10}N_4$, forms toothed needles or prisms, m. p. 202°.

2 : 5-*Diphenylpyrazine*-3-*carboxylic acid*, $C_{17}H_{12}O_2N_2$, forms white plates, m. p. 197° (losing carbon dioxide); the *sodium* salt ($+5H_2O$) was prepared. 6-*Hydroxy*-2 : 5-*diphenylpyrazine*-3-*carboxylic acid*, $C_{17}H_{12}O_3N_2$, crystallises in straw-yellow prisms, m. p. 263° (losing carbon dioxide). 6-*Hydroxy*-2 : 5-*diphenylpyrazine*, $C_{16}H_{12}ON_2$, forms compact prisms, m. p. 284°, and yields a *bromo*-derivative, $C_{16}H_{11}ON_2Br$, crystallising in bundles of slender, yellow needles, m. p. 245°.

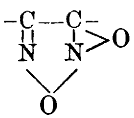
The author has prepared: (1) the compound described by Pinner (A., 1905, i, 476) as 3-hydroxy-1 : 4-diphenylpyrazine, m. p. 196—197°, by the action of ammonia on either phenylglyoxal or the sodium hydrogen sulphite compound of oximinoacetophenone (compare Pechmann, A., 1890, 51), and (2) the compound described by Japp and Knox (T., 1905, **87**, 703) as 3-keto-2 : 5-diphenyl-3 : 4-dihydropyrazine, by the action of gaseous hydrogen chloride on mandelonitrile (compare Minovici, A., 1899, i, 890). The two compounds thus prepared are found to be identical and they yield one and the same bromo-derivative, m. p. 200° (compare Minovici, *loc. cit.*).

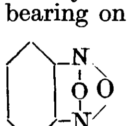
Further, the action of methylamine on either phenylglyoxal or the sodium hydrogen sulphite compound of oximinoacetone yields the methyl ether of the compound, m. p. 196—197°, this being identical with the ether obtained by Engler and Hassenkamp (A., 1885, 1223) by direct methylation of Pinner's so-called 3-hydroxy-1 : 4-diphenylpyrazine; since the author's method of preparation shows that this ether is undoubtedly an N-methyl derivative, Pinner's interpretation of the reaction giving the compound, m. p. 196—197°, and of its structure cannot be accepted. Moreover, the compound obtained by Japp and Knox by reducing 3-keto-2 : 5-diphenyl-3 : 4-dihydropyrazine by means of hydriodic acid and red phosphorus and regarded by them as 2 : 5-diphenyl-3 : 4-dihydropyrazine does not exhibit the properties of the dihydropyrazines (Gabriel and Lieck, A., 1908, i, 464).

The compound, m. p. 280°, obtained by Pinner (*loc. cit.*) by the action of ammonia on phenylglyoxal, this author regarded as 2-benzoyl-5-phenylglyoxaline, since, like all glyoxalines, it yields a methiodide (the 1-methyl-3-methiodide) which, when melted, loses methyl iodide and gives 2-benzoyl-5-phenyl-1-methylglyoxaline, and since the latter yields methylamine when heated with sodium hydroxide. The author finds, however, that Pinner's compound, m. p. 280°, and 6-hydroxy-2 : 5-diphenylpyrazine, m. p. 284°, yield one and the same bromo-derivative, m. p. 245°, and must be regarded as identical, Pinner's product being probably slightly impure. The pyrazinic structure the author attributes to the compound is confirmed by its behaviour towards hydriodic acid, by which it, like the other arylpyrazines obtained by the author, is converted into 2 : 5-diphenyl-3 : 6-dihydropyrazine. T. H. P.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. IV. The Condensation of Ethyl 3- and 5-Nitro-2-chlorobenzoates with Hydrazines. JAMES KENNER and ERNEST WITHAM (T., 1921, **119**, 1053—1058).

The Constitution of Furoxans (Glyoxime Peroxides). HEINRICH WIELAND (*Annalen*, 1921, **424**, 107—116).—The paper is occupied principally with a defence of the unsymmetrical formula (annexed) for furoxans, the arguments resting mainly on the facts established in previous investigations (compare A., 1908, i, 108; 1909, i, 609, 610; 1910, i, 784) on these substances. The fact that Green and Rowe (T., 1912, **101**, 2452; 1913, **103**, 897, 2023; 1918, **113**, 67) have proved that benzo*iso*oxadiazole is a symmetrically constituted substance is considered to have no bearing on the constitution of furoxans in general, since benzo*iso*oxadiazole belongs to a totally distinct class of compound. In fact the formula (annexed) deemed by Green and Rowe the most suitable expression for this substance is tantamount to regarding it as an internally coupled bis-nitroso-compound, a view justified by the chemistry of this and all aromatic ortho-dinitroso-compounds, but certainly not capable of extension to the simple furoxans investigated





by the author. There is, moreover, definite experimental proof of the dis-symmetry of furoxandicarboxylamide (A., 1909, i, 610).

An unstable form, m. p. 106—108°, of *phenylfuroxan* is described.

C. K. I.

Some New Tricyclic Bases. Tom Sidney Moore and Ida Doubleday (T., 1921, **119**, 1170—1175).

[The Uric Acids and Their Derivatives.] Heinrich Biltz (*Annalen*, 1921, **423**, 119—122. Compare A., 1910, i, 521, 526, 589, 594; 1911, i, 168, 240, 692, 693; 1912, i, 589; 1913, 166, 600, 1376; 1914, i, 23, 441, 586—592, 1093—1096; 1917, i, 286—300, 589—591; 1918, i, 455; 1919, 292—293; this vol., i, 590).—The author reviews the various parts of the subject dealt with in the accompanying papers (compare following abstracts) and appends references to his earlier researches on uric acid and its alkyl derivatives. C. K. I.

7-Methyluric Acid and its Derivatives. Heinrich Biltz, Karl Marwitzky, and Myron Heyn (*Annalen*, 1921, **423**, 123—146. Compare preceding abstract).—This paper deals with the formation and reactions of certain alkyl derivatives of 4 : 5-dihydroxy-7-methyl-4 : 5-dihydrouric acid, $\begin{matrix}\mathrm{NH\cdot CO{-}C(OH)\cdot NMe} \\ \mathrm{CO\cdot NH\cdot C(OH){-}NH}\end{matrix}\Big>\mathrm{CO}$, and its isomeride 5-hydroxy-7-methyl-ψ-uric acid,

$$\begin{matrix}\mathrm{NH\cdot CO{-}C(OH)\cdot NMe\cdot CO\cdot NH_2}, \\ \mathrm{CO\cdot NH\cdot CO}\qquad\qquad\qquad\quad\end{matrix}$$

neither of which, however, are as yet known.

Derivatives of the first of these substances are obtained by the regulated action of chlorine on 7-methyluric acid suspended in an appropriate alcohol. Thus, using methyl alcohol at the temperature of an ice-and-salt freezing mixture, there is obtained 4 : 5-*dimethoxy*-7-*methyl*-4 : 5-*dihydrouric acid*, which separates from water or methyl alcohol in dense four- or six-sided prisms, m. p. 211° (corr., decomp.). The *diethoxy*-derivative, prepared in a similar manner from 7-methyluric anhydride, ethyl alcohol, and chlorine, crystallises from ethyl alcohol in rhombic leaflets, m. p. 214—215° (corr., decomp.). Both the diethoxy- and dimethoxy-compounds are converted on reduction by stannous chloride and hydrochloric acid into 7-methyluric acid.

If the treatment with chlorine of ethyl alcoholic 7-methyluric anhydride is prolonged, or the reaction mixture is not well cooled, 4-*hydroxy*-5-*ethoxy*-7-*methyl*-4 : 5-*dihydrouric acid* is produced, which may also be obtained by warming the diethoxy-compound with hydrochloric acid; it crystallises from ethyl alcohol in rhombic leaflets, m. p. 214° (decomp.). On reduction at 100° with hydriodic acid, it gives 1-methylhydantoin, whilst on digesting at room temperature with methyl alcoholic hydrogen chloride it yields *methyl* 5-*methoxy*-1-*methylhydantoin*-5-*carboxylate*, $\begin{matrix}\mathrm{NH{-}CO} \\ \mathrm{CO\cdot NMe}\end{matrix}\Big>\mathrm{C(OH)\cdot CO_2Me}$, which crystallises in rhombic plates, m. p. 131° (corr.) and on reduction with hydriodic acid passes into 1-methylhydantoin. It was not found possible to obtain 4-hydroxy-5-methoxy-7-methyl-4 : 5-

dihydrouric acid by methods similar to those which yielded the hydroxy-ethoxy-acid.

When dry chlorine reacts with 7-methyluric acid in a mixture of glacial acetic acid and acetic anhydride, *5-chloro-7-methyl-Δ^4-isouric acid*, $\begin{matrix}\text{NH·CO–CCl·NMe}\\ | \qquad\quad | \\ \text{CO·NH·C=\!=\!=N}\end{matrix}\!\!>\!\text{CO}$, is produced as an unstable substance having no definite temperature of decomposition, and passing on reduction by hydriodic acid or by stannous chloride into 7-methyluric acid. 4 : 5-Dimethoxy-7-methyl-4 : 5-dihydrouric acid is formed when it is treated with methyl alcohol, but the product obtained on treating with water is not 4 : 5-dihydroxy-7-methyl-4 : 5-dihydrouric acid, but 4 : 5-dihydroxy-9-methyl-4 : 5-dihydroxyuric acid, a complete fission of the molecule to alloxan and methylcarbamide having taken place intermediately. Attempts to produce 4 : 5-dihydroxy-7-methyl-4 : 5-uric acid (formula above) by the direct action of chlorine on 7-methyluric acid in the presence of water led to the formation of substances containing chlorine.

The action of halogen on 7-methyl-ψ-uric acid leads in general to the production of derivatives or analogues of 5-hydroxy-7-methyl-ψ-uric acid (formula above). Thus treatment with chlorine in the presence of glacial acetic acid at 0° gives *5-chloro-7-methyl-ψ-uric acid*, which separates in association with a molecule of acetic acid and is too unstable to be recrystallised. On reduction by means of stannous chloride and hydrochloric acid, it yields 7-methyl-ψ-uric acid, but on reduction by hydriodic acid it gives 3-methylhydantoin, a complete fission of the molecule to alloxan and methylcarbamide having occurred during the reaction. A similar decomposition is brought about by the action of water, for under some conditions the product is 4 : 5-dihydroxy-9-methyl-4 : 5-dihydrouric acid, whilst under others it is an additive compound of methylcarbamide and alloxan. On digesting 5-chloro-7-methyl-ψ-uric acid with methyl alcohol at the ordinary temperature *5-methoxy-7-methyl-ψ-uric acid* is obtained, which may also be prepared directly from 7-methyl-ψ-uric acid by the action of bromine and methyl alcohol at 0°; it decomposes at about 176° (corr.), and undergoes deep-seated change when the attempt is made to convert it into the isomeric uric acid by the action of dilute mineral acids. The corresponding *ethoxy*-derivative (decomp. 165°, corr.), prepared from 7-methyl-ψ-uric acid, bromine, and ethyl alcohol, changes readily, however, into 4-hydroxy-5-ethoxy-7-methyl-4 : 5-dihydrouric acid when treated with dilute hydrochloric acid.

Experimental details are given for the preparation of 7-methyl-ψ-uric acid and 7-methyluric acid from 7-methyluramil, and of 7-methyluric acid from uric acid and formaldehyde. 7-Methyluric acid is soluble in 199 parts by weight of boiling water. Its monoacetyl derivative, obtained by digesting with acetic anhydride, separates from water in plates decomposing above 315°. C. K. I.

7-Ethyluric Acid and its Derivatives. HEINRICH BILTZ, KARL MARWITZKY, and MYRON HEYN (*Annalen*, 1921, **423**, 147—159. Compare preceding abstract).—7-Ethyluramil, which may be

prepared by condensing dialuric acid with ethylamine, reacts with potassium cyanate, giving a good yield of 7-ethyl-ψ-uric acid or 7-ethyluric acid, according to the experimental conditions employed. 7-*Ethyl-ψ-uric acid* separates from water in four-sided domed prisms containing $1H_2O$ which is given up at 130°, the anhydrous acid sintering at 202° and decomposing at 208°; it is converted by the usual means into 7-ethyluric acid, which separates from water in four-sided prisms, decomp. 361—362° (uncorr.). *Ethylamine dialurate*, m. p. 286° (decomp.), is also described.

4 : 5-*Dimethoxy-7-ethyl-4 : 5-dihydrouric acid*, obtained from 7-ethyluric acid by the action of chlorine and methyl alcohol, separates from this solvent in small, quadratic plates, m. p. 206° (corr., decomp.), and on reduction by means of stannous chloride is reconverted into 7-ethyluric acid. The 4 : 5-*diethoxy*-derivative prepared in a similar manner separates from ethyl alcohol in minute crystals, m. p. 193° (corr., decomp.), and yields 7-ethyluric acid on reduction by stannous chloride. It is converted by hydrochloric acid into *4-hydroxy-5-ethoxy-7-ethyl-4 : 5-dihydrouric acid*, the principal product of the action of an excess of chlorine on 7-ethyluric acid suspended in a limited quantity of ethyl alcohol. This acid has m. p. 208° (corr., decomp.), is converted by hydriodic acid at 100° into 1-ethylhydantoin, which separates from ethyl acetate in large, rhombic tablets sintering at 80° and decomposing at 104° (corr.) (compare Heintz, *Annalen*, 1865, **133**, 65), and by methyl-alcoholic hydrogen chloride into *methyl 5-methoxy-1-ethyl-hydantoin-5-carboxylate*, which separates from methyl alcohol in large, rhombic tablets, m. p. 146°, and on reduction by hydriodic acid yields 1-ethylhydantoin.

5-Chloro-7-ethyl-Δ^4-*iso*uric acid and 5-chloro-7-ethyl-ψ-uric acid were not obtained by the methods which yielded the corresponding 7-methyl compounds; the products isolated were amorphous and apparently contained alloxan, since they yielded alloxantin on reduction by stannous chloride. However, *5-methoxy-7-ethyl-ψ-uric acid* is easily prepared by the action of bromine and methyl alcohol on anhydrous 7-ethyl-ψ-uric acid at the temperature of a freezing mixture. This substance, which is obtained as plates, decomp. 167—168°, undergoes deep-seated decomposition when treated with hydrochloric acid, but the 5-*ethoxy*-derivative, plates, decomp. 118—120°, prepared in a similar manner using ethyl alcohol, is readily isomerised by hydrochloric acid to 4-hydroxy-5-ethoxy-7-ethyl-4 : 5-dihydrouric acid.

On treating 7-ethyluric acid with chlorine in the presence of water there is obtained a substance, $C_7H_9O_5N_4Cl$, m. p. 163° (decomp.). This is probably the *monohypochlorite* of 4 : 5-dihydroxy-7-ethyl-4 : 5-dihydrouric acid, since it eliminates hypochlorous acid on digesting with alcohol and is converted by concentrated hydrochloric acid into 1-ethylcaffolide with the elimination of ammonium chloride.

$$\begin{array}{l}\mathrm{NH\cdot CO\cdot C(OH)\cdot NEt}\\ \mathrm{CO\cdot NH\cdot C(OCl)\cdot NH}\end{array}\!\!>\mathrm{CO} \longrightarrow \begin{array}{l}\mathrm{NH\cdot CO}\\ \mathrm{CO{-}O}\end{array}\!\!>\mathrm{C}<\!\!\begin{array}{l}\mathrm{NEt\cdot CO}\\ \mathrm{CO{-}NH}\end{array} + \mathrm{NH_4Cl}.$$

1-*Ethylcaffolide* separates from water in rhombic tablets which sinter at 200° and melt at 210—211° (decomp.). C. K. I.

Derivatives of 7 : 9-Dimethyluric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1921, **423**, 159—177. Compare preceding abstract).—4 : 5-Dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid is noteworthy on account of its ease of formation and stability (contrast its analogues, preceding abstracts). It is obtained directly from 7 : 9-dimethyluric acid by the action of chlorine and water at 0°, and by hydrolysis of the ethoxy- and methoxy-derivatives described below, and is identical with the synthetical product prepared from alloxan and *s*-dimethylcarbamide.

4 : 5-*Dimethoxy*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid* is prepared by passing chlorine into a suspension of 7 : 9-dimethyluric acid in methyl alcohol at the temperature of a freezing mixture, and forms rhombic or six-sided plates, m. p. 187° (corr., decomp.). Stannous chloride and hydrochloric acid convert it into 7 : 9-dimethyluric acid, and methyl-alcoholic hydrogen chloride into *methyl* 5-*methoxy*-1 : 3-*dimethylhydantoin*-5-*carboxylate*, thick prisms, m. p. 72°. When condensed with *s*-dimethylcarbamide in the presence of hydrogen chloride at 150°, 1 : 3 : 1′ : 3′-tetramethyl*spiro*dihydantoin is produced. 4 : 5-*Diethoxy*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, rhombs, m. p. 193° (corr., decomp.), is prepared like the dimethoxy-compound and behaves similarly on reduction by stannous chloride.

4-*Hydroxy*-5-*methoxy*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid* obtained when the dimethoxy-compound is warmed with dilute hydrochloric acid, crystallises in hexagonal plates, m. p. 184° (corr.), on reduction by hydriodic acid yields 1 : 3-dimethylhydantoin and on hydrolysis by sulphuric acid the dihydroxy-derivative. The 4-*hydroxy*-5-*ethoxy*-compound is prepared in the same way from the diethoxy-derivative and may be isolated as a by-product in the preparation of that substance. It crystallises in four-sided, domed prisms, m. p. 185° (corr.), and closely resembles the hydroxy-methoxy-compound in its reactions.

When a suspension of 7 : 9-dimethyluric acid in chloroform is treated with chlorine 4 : 5-*dichloro*-7 : 9-*dimethyl*-4 : 5-*dihydrouric acid* is obtained, which sinters at 115° and decomposes at 126—130°; water reacts with it to form the dihydroxy-compound, methyl alcohol and ethyl alcohol to give the dimethoxy- and diethoxy-derivatives respectively, and stannous chloride in hydrochloric acid to yield 7 : 9-dimethyluric acid.

Full experimental details are given for the preparation of this acid from uric acid (by way of 2 : 6-dichloro-8-hydroxypurine). It dissolves in 380 parts of boiling water and on methylation in alkaline solution by means of methyl sulphate yields 1 : 7 : 9-trimethyluric acid. C. K. I.

Derivatives of 1 : 7 : 9-Trimethyluric Acid. HEINRICH BILTZ and HANS KRZIKALLA (*Annalen*, 1921, **423**, 177—184. Compare preceding abstract).—The principal characteristic of 1 : 7 : 9-trimethyluric acid appears to be the remarkable ease with which

it is converted into 1 : 3 : 7-trimethylcaffolide ("allocaffeine"), $\begin{array}{l} \text{NMe}\cdot\text{CO} \\ \text{CO---O} \end{array}\!\!>\!C\!<\!\!\begin{array}{l} \text{NMe}\cdot\text{CO} \\ \text{CO---NMe} \end{array}$, by the action of chlorine.

The caffolide is formed, for example, in 75% yield when chlorine is passed through a suspension of 1 : 7 : 9-trimethyluric acid in water. When methyl alcohol is used in place of water, the product is a mixture of 1 : 3 : 7-trimethylcaffolide and 4 : 5-*di-methoxy*-1 : 7 : 9-*trimethyl*-4 : 5-*dihydrouric acid*. The latter crystallises in hexagonal tablets, m. p. 152° (corr.), and on reduction either by sodium amalgam or by hydriodic acid is reconverted into 1 : 7 : 9-trimethyluric acid. 4 : 5-*Diethoxy*-1 : 7 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, rhombic or hexagonal tables, m. p. 169° (corr.), is obtained along with 1 : 3 : 7-trimethylcaffolide by the action of chlorine on a suspension of 1 : 7 : 9-trimethyluric acid in ethyl alcohol, and is converted into trimethylcaffolide by hot or cold, concentrated or dilute, hydrochloric or acetic acids.

4 : 5-*Dichloro*-1 : 7 : 9-*trimethyl*-4 : 5-*dihydrouric acid* appears to be too unstable to be capable of isolation, but evidence of its formation, when chlorine is passed into a suspension of 1 : 7 : 9-trimethyluric acid in chloroform, was obtained by isolating the dimethoxy-derivative after adding methyl alcohol and pyridine.

C. K. I.

The Preparation of 1 : 3-Dimethyl-ψ-uric Acid and 1 : 3-Dimethyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Annalen*, 1921, **423**, 185—192. Compare preceding abstract).—The authors describe a new method of obtaining 1 : 3-dimethyluric acid, suitable in every way for the preparation of large amounts of this substance, which depends on the principle that when a ψ-uric acid is treated with methyl sulphate in alkaline solution only the cyclic imino-groups become methylated. The process consists, therefore, in converting uric acid by means of chlorine into 5-chloro-ψ-uric acid, reducing this to ψ-uric acid, then methylating by methyl sulphate, and, finally, converting the 1 : 3-dimethyl-ψ-uric acid so obtained into 1 : 3-dimethyluric acid by boiling with hydrochloric acid.

When uric acid is directly methylated by means of methyl sulphate, the product, although by no means pure 1 : 3-dimethyluric acid, contains a considerable proportion of this substance.

C. K. I.

Methylation of 7-Methyl-ψ-uric Acid and 7-Ethyl-ψ-uric Acid. HEINRICH BILTZ and GERTRUD ZELLNER (*Annalen*, 1921, **423**, 192—200. Compare preceding abstract).—The method indicated in the abstract immediately preceding this of introducing methyl groups into the 1- and 3-positions by methylating the corresponding ψ-uric acids in alkaline solution by means of methyl sulphate has now been extended to the preparation of 1 : 3 : 7-trimethyluric acid and 1 : 3-dimethyl-7-ethyluric acid from 7-methyl-ψ-uric and 7-ethyl-ψ-uric acids respectively.

1 : 3 : 7-Trimethyl-ψ-uric acid forms a sodium salt,

$C_8H_{11}O_4N_4Na,H_2O$. Treatment with chlorine in the presence of a mixture of acetic acid and acetic anhydride converts it into 5-*chloro*-1 : 3 : 7-*trimethyl-ψ-uric acid*, strongly hygroscopic four-sided leaflets, m. p. 180° (corr., decomp.), which on digesting with methyl alcohol yields 5-*methoxy*-1 : 3 : 7-*trimethyl-ψ-uric acid*, and with ethyl alcohol the corresponding *ethoxy-acid*, a substance which separates from alcohol in slender needles, m. p. 145° (decomp.). When the chloro-acid is reduced by means of sodium amalgam it yields 1 : 3 : 7-trimethyl-ψ-uric acid, but when hydriodic acid is used the product is 1 : 3 : 7-trimethyluric acid.

1 : 3-*Dimethyl*-7-*ethyluric acid*, formed when the crude methylation product obtained from 7-ethyl-ψ-uric acid is boiled with hydrochloric acid, crystallises in flat prisms, m. p. 283° (corr., decomp.). Chlorine in the presence of methyl alcohol converts it into 4 : 5-*dimethoxy*-1 : 3-*dimethyl*-7-*ethyl*-4 : 5-*dihydrouric acid*, which crystallises in rhombs, m. p. 189°. C. K. I.

8-Thiouric Acids and *iso*Xanthines containing Alkyl Groups in Position 9. HEINRICH BILTZ and KARL STRUFE [and in part ERNST TOPP, MYRON HEYN, and RUDOLF ROBL] (*Annalen*, 1921, **423**, 200—226. Compare preceding abstract).—As a preliminary step to the preparation in quantity of uric acids alkylated in position 9, the reaction of Boehringer & Söhne (A., 1901, i, 770), whereby-Δ^7-*iso*xanthines alkylated in this position are obtained starting from a uramil and an alkylthiocarbimide, has been re-examined and applied to several new cases.

The reaction between 9-methyl-8-thiouric acid and nitrous acid leading to the formation of 9-methyl-Δ^7-*iso*xanthine has been examined in some detail and an orange intermediate product, $C_6H_{10}O_4N_6$ (probable constitution $\begin{matrix} NH\cdot CO\cdot C\cdot N(NO) \\ CO\cdot NH\cdot C\text{---}NMe \end{matrix}\!\!>\!CH\cdot O\cdot NH_4$), isolated. Bromination of 9-methyl-Δ^7-*iso*xanthine in glacial acetic acid at 100° leads to the formation of a *perbromide*, $C_6H_5O_2N_4Br,Br_2$, which at 200° loses bromine, yielding 8-*bromo*-9-*methyl*-Δ^7-iso*xanthine*, m. p. 290° (decomp.), a substance in which the bromine is very firmly bound; it may also be obtained from the perbromide by hydrolysis with aqueous ammonia. Methyl sulphate reacts with the sodium salt of 9-methyl-Δ^7-*iso*xanthine to form a dimethyl-*iso*xanthine, probably 3 : 9-*dimethyl*-Δ^7-iso*xanthine*, lustrous needles, m. p. 364° (decomp.), (*aurichloride*, $C_7H_8O_2N_4,HAuCl_4$, m. p. 297—300° decomp.), which on bromination in acetic acid loses a methyl group and yields the above-mentioned 8-bromo-9-methyl-Δ^7-*iso*xanthine.

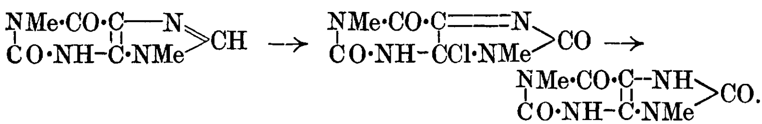
The following xanthines and intermediate products obtained in their preparation are new: 9-*ethyl*-8-*thio-ψ-uric acid*, six-sided leaflets, m. p. 189—190° (corr., decomp.), 9-*ethyl*-8-*thiouric acid*, small leaflets of irregular shape, m. p. 350° (corr., decomp.), 1 : 9-*dimethyl*-8-*thio-ψ-uric acid*, six-sided tables, m. p. 204° (corr., decomp.), 1 : 9-*dimethyl*-8-*thiouric acid*, four-sided prisms, m. p. 370° (corr., decomp.), 1 : 9-*dimethyl*-Δ^7-iso*xanthine*, lustrous needles, m. p. 350° (corr., decomp.), (*aurichloride*, $C_7H_8O_2N_4,HAuCl_4$, m. p.

255°, decomp.), 1-*methyl*-9-*ethyl*-8-*thio*-ψ-*uric acid*, rhombic tablets, m. p. 195° (corr., decomp.), 1-*methyl*-9-*ethyl*-8-*thiouric acid*, lustrous leaflets, m. p. 367° (corr., decomp.), 1-*methyl*-9-*ethyl*-Δ^7-iso*xanthine*, needles, m. p. 335° (corr., decomp.), 1 : 3 : 9-*trimethyl*-8-*thio*-ψ-*uric acid*, four-sided prisms, m. p. 208—209° (corr., decomp.), 1 : 3 : 9-*trimethyl*-8-*thiouric acid*, sinters at 325, and decomposes at 355° (corr.), 1 : 3 : 9-*trimethyl*-Δ^7-iso*xanthine* (iso*caffeine*), needles, m. p. 285—287° (corr., decomp.), 1 : 3-*dimethyl*-9-*ethyl*-8-*thio*-ψ-*uric acid*, four-sided, right prisms, m. p. 195° (corr., decomp.), 1 : 3-*dimethyl*-9-*ethyl*-8-*thiouric acid*, needles, m. p. 277° (corr., decomp.), and 1 : 3-*dimethyl*-9-*ethyl*-Δ^7-iso*xanthine*, slender needles, m. p. 227—228° (corr., decomp.).

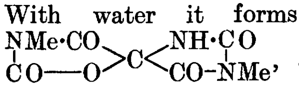
1 : 3-Dimethyluramil undergoes a unique type of condensation with methylcarbimide, the product being tetramethylhydurilic acid.

C. K. I.

Derivatives of 1 : 9-Dimethyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1921, **423**, 227—237. Compare preceding abstract).—The synthesis of 1 : 9-dimethyl-Δ^7-*iso*-xanthine opens the way to the preparation of a large number of derivatives of 1 : 9-dimethyluric acid and 1 : 9-dimethyl-ψ-uric acid. Thus on chlorinating 1 : 9-dimethyl-Δ^7-*iso*xanthine in glacial acetic acid 4-chloro-1 : 9-dimethyl-Δ^5-*iso*uric acid is formed, and on reduction by means of stannous chloride and hydrochloric acid or by hydriodic acid yields 1 : 9-dimethyluric acids,



4 : *Chloro*-1 : 9-*dimethyl*-Δ^5-iso*uric acid* is a hygroscopic, crystalline substance which reacts energetically with water and alcohols. With water it forms 3 : 7-*dimethylcaffolide* (isoapo*caffeine*),



and with methyl and ethyl alcohols 5-*methoxy*-1 : 9-*dimethyl*-ψ-*uric acid* and 5-*ethoxy*-1 : 9-*dimethyl*-ψ-*uric acid* respectively. The methoxy-acid forms short, four-sided prisms, m. p. 203° (corr., decomp.), and on reduction by hydriodic acid in glacial acetic acid in the cold yields 1 : 9-dimethyl-ψ-uric acid, whilst the ethoxy-acid crystallises in elongated leaflets, m. p. 200° (corr., decomp.), and is converted by hydriodic acid at 100° into 1 : 9-dimethyluric acid. 1 : 9-*Dimethyl*-ψ-*uric acid*, needles, m. p. 252° (corr., decomp.), on chlorination in the presence of methyl alcohol, regenerates the methoxy-compound from which it is prepared.

When concentrated hydrochloric acid is added to a solution of 5-methoxy-1 : 9-dimethyl-ψ-uric acid in sodium hydroxide an isomeric change occurs. The dicyclic product, however, is not 4-hydroxy-5-methoxy-1 : 9-dimethyl-4 : 5-dihydrouric acid but 4-hydroxy-5-methoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid, and is

identical with the product obtained by methylating 4-hydroxy-5-methoxy-3-methyl-4 : 5-dihydrouric acid by methyl sulphate and sodium hydroxide. It is clear, therefore, that of the two carbonyl groups (marked *) adjacent to the side chain in 5-methoxy-1 : 9-dimethyl-ψ-uric acid, $CO{<}{\substack{NMe\cdot CO^*\\ NH-CO_*}}{>}C(OMe)\cdot NH\cdot CO\cdot NHMe$, that next the methyl-bearing nitrogen atom is the one concerned in the formation of the second ring. This is also the case when 5-ethoxy-1 : 9-dimethyl-ψ-uric acid is employed. 4-*Hydroxy*-5-*methoxy*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid* forms domed prisms, m. p. 204° (corr., decomp.), and 4-*hydroxy*-5-*ethoxy*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, which may also be prepared by methylating 4-hydroxy-5-ethoxy-3-methyl-4 : 5-dihydrouric acid by the use of methyl sulphate, is obtained as leaflets, m. p. 174° (corr.).

C. K. I.

Derivatives of 1-Methyl-9-ethyluric Acid. HEINRICH BILTZ and KARL STUFE (*Annalen*, 1921, **423**, 237—241. Compare preceding abstract).—1-Methyl-9-ethyl-Δ^7-*iso*xanthine is converted successively into 4-*chloro*-1-*methyl*-9-*ethyl*-Δ^5-iso*uric acid* and 1-methyl-9-ethyluric acid by the method employed (preceding abstract) in the case of the 1 : 9-dimethyl compounds. The chloro-compound, hexagonal prisms, m. p. 180° (corr., decomp.), is much more stable in this instance and can be recrystallised for analysis. 1-*Methyl*-9-*ethyluric acid* melts above 360° (decomp.), is sparingly soluble in water, and on chlorination in glacial acetic acid yields the above chloro*iso*uric acid.

Another contrast with the 1 : 9-dimethyl series consists in the fact that it is possible to isolate the dimethoxy-acid from the product of the reaction between 4-chloro-1-methyl-9-ethyl-Δ^5-*iso*-uric acid and methyl alcohol. If the chloro-acid be treated with methyl alcohol and one drop of pyridine without external cooling the chief product is 5-*methoxy*-1-*methyl*-9-*ethyl*-ψ-*uric acid*, four-sided prisms, m. p. 182° (corr., decomp.), but if the reaction be carried out at 0°, 4 : 5-*dimethoxy*-1-*methyl*-9-*ethyl*-4 : 5-*dihydrouric acid*, leaflets, m. p. 148° (corr.), is obtained. This acid, however, is easily converted into the ψ-uric acid by warming with dilute acids.

5-*Ethoxy*-1-*methyl*-9-*ethyl*-ψ-*uric acid* separates from water in leaflets, m. p. 176° (corr., decomp.). C. K. I.

Derivatives of 1 : 3 : 9-Trimethyluric Acid. HEINRICH BILTZ and KARL STRUFE (*Annalen*, 1921, **423**, 442—454. Compare preceding abstract).—The preparation of 1 : 3 : 9-trimethyluric acid is attended with some difficulty, as the direct methylation of 1 : 3-dimethyluric acid (through the lead salt) leads to the formation of a mixture of acids, and two new methods of obtaining this trimethyluric acid in a pure condition are described. The first of these starts from 1 : 3 : 9-trimethyl*iso*xanthine, which is brominated, and the 8-*bromo*-derivative, m. p. 256° (corr., decomp.), so obtained converted by boiling with 10% alcoholic potassium

hydroxide into 8-*methoxy*-1 : 3 : 9-*trimethyl*iso*xanthine*, which crystallises in silky needles, m. p. 230° (corr., decomp.), and on hydrolysis by means of hydrochloric acid yields 1 : 3 : 9-trimethyluric acid. The second synthesis consists in methylating 9-methyl-ψ-uric acid by methyl sulphate. The product is 1 : 3 : 9-*trimethyl-ψ-uric acid*, m. p. 220° (corr., decomp.), which on treatment with hydrochloric acid passes into the uric acid. Pure 1 : 3 : 9-trimethyluric acid melts at 347° (corr., decomp.), and crystallises in the rhombic system.

4-*Chloro*-1 : 3 : 9-*trimethyl*-Δ^5-iso*uric acid* is obtained by the action of chlorine on 1 : 3 : 9-trimethyluric acid as an unstable hygroscopic, micro-crystalline substance, m. p. 170° (decomp.), which on reduction by hydriodic acid at the ordinary temperature yields 1 : 3 : 9-trimethyluric acid, and on digesting with methyl alcohol is converted into 5-*methoxy*-1 : 3 : 9-*trimethyl-ψ-uric acid*. This may also be prepared by treating 1 : 3 : 9-trimethyluric acid or 1 : 3 : 9-trimethyl-ψ-uric acid directly with chlorine in the presence of methyl alcohol. It crystallises in elongated prisms, m. p. 184° (corr., decomp), and on reduction by hydriodic acid at ordinary temperatures yields 1 : 3 : 9-trimethyl-ψ-uric acid. 5-*Ethoxy*-1 : 3 : 9-*trimethyl-ψ-uric acid*, six-sided prisms, m. p. 182° (corr., decomp.), may be obtained by the same general reactions and has similar properties.

When a solution in aqueous sodium hydroxide of 5-methoxy-1 : 3 : 9-trimethyl-ψ-uric acid is acidified by hydrochloric acid the precipitate consists of 4-*hydroxy*-5-*methoxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, which is also obtained when 4-hydroxy-5-methoxy-1 : 3-dimethyl-4 : 5-dihydrouric acid is treated with methyl sulphate. It crystallises in four-sided prisms, m. p. 194° (corr., decomp.); 4-*hydroxy*-5-*ethoxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, prepared by similar means, forms elongated leaflets, m. p. 138° (corr.). C. K. I.

3 : 9-Dimethyluric Acid and its Derivatives. HEINRICH BILTZ and HANS KRZIKALLA (*Annalen*, 1921, **423**, 255—281. Compare preceding abstract).—3 : 9-Dimethyluric acid, prepared by the action of methyl sulphate on the dipotassium salt of uric acid, crystallises in bevelled prisms or spear-shaped leaflets which turn yellow at 360° and decompose vigorously at 410—420°. The acid is soluble in 300 parts of boiling water, yields with acetic anhydride a *monoacetyl* derivative, m. p. above 300°, and with methyl sulphate and sodium hydroxide tetramethyluric acid.

4 : 5-*Dimethoxy*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, prisms, m. p. 223° (corr., decomp.), obtained by the action of chlorine at the temperature of a freezing mixture on 3 : 9-dimethyluric acid in the presence of methyl alcohol, is reduced by sodium amalgam to 3 : 9-dimethyluric acid but by hydriodic acid at 100° to 1 : 9-dimethyluric acid. 1 : 9-Dimethyl-ψ-uric acid, which is obtained when hydriodic acid is allowed to react at room temperature, is evidently an intermediate product in the conversion of 3 : 9-dimethyluric acid into its 1 : 9-isomeride by this means :

$$\begin{array}{l}NH-CO\\ CO\quad C-NH\\ NMe\cdot C\cdot NMe\end{array}\!\!>CO \longrightarrow \begin{array}{l}NH-CO\\ CO\quad C(OMe)-NH\\ NMe\cdot C(OMe)\cdot NMe\end{array}\!\!>CO \longrightarrow$$

$$\begin{array}{l}NH-CO\\ CO\quad CH\cdot NH\cdot CO\cdot NHMe\\ NMe\cdot CO\end{array} \longrightarrow \begin{array}{l}NH-C\cdot NMe\\ CO\quad C-NH\\ NMe\cdot CO\end{array}\!\!>CO$$

4 : 5-*Diethoxy*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, which crystallises in prisms, m. p. 238° (corr. decomp.), belonging to the triclinic system, is formed analogously to the dimethoxy-compound and has similar properties.

Partial hydrolysis occurs when 4 : 5-dimethoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid is boiled with dilute hydrochloric acid. The product, 4-hydroxy-5-methoxy-3 : 9-dimethyl-4 : 5-dihydrouric acid, is identical with that obtained by methylation of 4-hydroxy-5-methoxy-3-methyl-4 : 5-dihydrouric acid or by ring-closure of 5-methoxy-1 : 9-dimethyl-ψ-uric acid. Similar relationships subsist between the corresponding ethoxy-compounds. With methyl alcoholic hydrogen chloride, the decomposition is more profound and the syrupy product on treatment with ammonia yields 5-*methoxy*-3-*methylhydantoin*-5-*carboxylamide*, $\begin{array}{l}CO\cdot NH\cdot C(OMe)\cdot CO\cdot NH_2,\\ NMe-\!\!-CO\end{array}$

m. p. 208—210° (corr., decomp.). The free dihydroxy-compound may, however, be obtained directly from 3 : 9-dimethyluric acid by chlorination in the presence of water. The immediate product is the *monohypochlorite*, $C_7H_9O_5N_4Cl$, of this glycol, m. p. 175° (corr., decomp.), this substance undergoing hydrolysis by water at 80°, yielding 4 : 5-*dihydroxy*-3 : 9-*dimethyl*-4 : 5-*dihydrouric acid*, which crystallises in four-sided prisms, m. p. 198—199° (corr., decomp.), and undergoes several remarkable decompositions. Thus on reduction by means of hydriodic acid it is converted into 3-methylhydantoin. On dissolving it in aqueous sodium hydroxide and adding concentrated hydrochloric acid, 3-*methylcaffolide* is precipitated as a crystalline material, m. p. 220 (corr., decomp.), which on boiling with water is hydrolysed to 5-*hydroxy*-3-*methylhydantoin*-5-*carboxylamide*:

$$\begin{array}{l}CO-NH\\ NMe\cdot CO\end{array}\!\!>C<\!\!\begin{array}{l}CO\cdot NH\\ O-CO\end{array} \longrightarrow \begin{array}{l}CO-NH\\ NMe\cdot CO\end{array}\!\!>C(OH)\cdot CO\cdot NH_2.$$

The latter separates from water in rhombic or six-sided plates, with $1H_2O$, which is evolved at 100°, the anhydrous residue melting at 178—180° (corr., decomp.). Finally, either the glycol or its hypochlorous ester when warmed with concentrated sulphuric acid yields 1 : 3-*dimethyl*spiro*dihydantoin*, m. p. 264—265° (corr., decomp.), which may be converted into the known tetramethyl*spiro*dihydantoin by treating its silver salt with methyl iodide. It can also be prepared directly from 3 : 9-dimethyluric acid by chlorination in the presence of glacial acetic acid.

Chlorination of 1 : 9-dimethyl-ψ-uric acid in the presence of glacial acetic acid leads to the formation of 5-*chloro*-1 : 9-*dimethyl*-ψ-*uric acid*, which sinters at 155° and decomposes at 180° (corr.), on reduction by means of hydriodic acid, regenerates 1 : 9-

dimethyl-ψ-uric acid, and on treatment with methyl and ethyl alcohols is converted into 5-methoxy-1 : 9-dimethyl-ψ-uric and 5-ethoxy-1 : 9-dimethyl-ψ-uric acids respectively. C. K. I.

The Action of Carbamide and of Substituted Carbamides on Alloxan and its Methyl Derivatives. HEINRICH BILTZ (*Annalen*, 1921, **423**, 282—295. Compare A., i, 1910, 522, 523; 1912, 589; 1914, 441, 586, and preceding abstract).—The condensations of alloxan, methylalloxan, and dimethylalloxan with carbamide, methylcarbamide, and *s*-dimethylcarbamide, mostly already described, are collected together and discussed in some detail.

It is considered that the initial condensation product (whether in any particular instance it can be isolated or not) is a glycol, and the condensation of methylalloxan with methylcarbamide, now described for the first time, is no exception to this rule. It may happen that the glycol is unstable under the conditions of its formation; if this be so the product isolated may be the caffolide formed by its decomposition. Thus under certain conditions the condensation of methylcarbamide with methylalloxan yields a mixture of 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid and 3 : 7-dimethylcaffolide ("*isoapo*caffeine," this vol., i, 612), whilst in other circumstances 3 : 7-dimethylcaffolide is the sole crystalline product.

One of the principal generalisations arrived at from a consideration of these examples is that the attachment of a second ring to a monomethylated alloxan ring takes place in such a way that of the three adjacent carbonyl groups in alloxan that nearest the methyl-bearing nitrogen atom remains unaffected. The formation of 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid mentioned above is an exception to this rule, which, nevertheless, embraces a considerable number of examples, and is generally in harmony with the course followed by ring-closure of the unsymmetrically substituted ψ-uric acids.

Alloxan (monohydrate) condenses with thiocarbamide when the two substances are warmed together in water. The product, which crystallises in four-sided prisms having no very definite decomposition temperature, has the empirical composition and apparently consists of 4 : 5-dihydroxy-4 : 5-dihydro-8-thiouric acid,

$$\begin{array}{l} NH\cdot CO-C(OH)\cdot NH \\ CO\cdot NH\cdot C(OH)\cdot NH \end{array}\!\!>CS.$$

C. K. I.

1 : 3-Diethylhydantoin. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1921, **423**, 295—296. Compare preceding abstract).—The formation of 1 : 3-dimethylhydantoin by the action of hydriodic acid on 4 : 5-dihydroxy-7 : 9-dimethyl-4 : 5-dihydrouric acid appears to point to the existence of a convenient general method of preparing alkylated hydantoins since the necessary glycols are easily obtained by the condensation of alloxan with the appropriate substituted carbamides. As an extension of this reaction, 1 : 3-*diethylhydantoin* has been prepared from the glycol obtained by condensing alloxan with *s*-diethylcarbamide. It is noteworthy as being a liquid at ordinary temperatures, b. p. 260—261°/754 mm. C. K. I.

1 : 3 : 7 : 7-Tetramethyluramil. HEINRICH BILTZ and GERTRUD ZELLNER (*Annalen*, 1921, **423**, 297—300. Compare preceding abstract).—The methylation, by means of methyl sulphate and sodium hydroxide, of 7-methyluramil and of 7 : 7-dimethyluramil leads to the formation of the same tetramethyluramil, which must therefore have the formula, $CO<\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>CHNMe_2$. It crystallises from absolute ethyl alcohol in bevel-end tablets, m. p. 230—232° (corr., decomp.), but from water as long, pointed needles consisting of the monohydrate, m. p. 225° (corr., decomp.). It is practically without acidic properties, but, on the other hand, is notably basic, yielding a hydrobromide, a nitrate, and a perchlorate with the appropriate mineral acids. C. K. I.

Derivatives of Alloxanic Acid (5-Hydroxyhydantoin-5-carboxylic Acid). HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1921, **423**, 301—317. Compare preceding abstract).—A number of derivatives of alloxanic acid have been prepared and their decompositions studied.

5-Methoxy-ψ-uric acid, as well as 4 : 5-dimethoxy-4 : 5-dihydrouric acid, yields methyl 5-methoxyhydantoin-5-carboxylate on digesting with methyl alcoholic hydrogen chloride, and the methoxy-ester on treatment with aqueous barium hydroxide at 80° is converted into alloxanic acid, $CO<\begin{matrix}NH\cdot C(OH)\cdot CO_2H\\NH\cdot CO\end{matrix}$. Aqueous ammonia converts the methoxy-ester into the corresponding amide, which may also be prepared directly from 5-methoxy-ψ-uric acid by evaporation on a water-bath with the same reagent. The latter reaction takes place in two stages; 4-hydroxy-5-methoxy-4 : 5-dihydrouric acid is formed intermediately and can be isolated by observing due precautions. 5-Methoxyhydantoin-5-carboxylamide on reduction by means of hydriodic acid yields hydantoin and on hydrolysis by boiling aqueous barium hydroxide undergoes fission into mesoxalic acid and carbamide; the anhydrous substance melts at 180—182° (corr., decomp.), but on crystallising from water a monohydrate, m. p. 140—145° (corr.), separates in double pyramids. 5-*Methoxyhydantoin*-5-*carboxymethylamide*, double pyramids or six-sided tablets, m. p. 177—178° (corr.), and 5-*methoxyhydantoin*-5-*carboxyethylamide*, flat prisms, m. p. 84—85° when monohydrated, m. p. 156° (corr.), when anhydrous, are prepared from 5-methoxy-ψ-uric acid by evaporating with aqueous methylamine and ethylamine respectively.

5-Ethoxy-ψ-uric acid on boiling with water or on evaporating with aqueous ammonia at ordinary temperatures yields 4-*hydroxy*-5-*ethoxy*-4 : 5-*dihydrouric acid*, rhombic or six-sided tablets, m. p. 208° (corr., decomp).; this when evaporated on a water-bath with aqueous ammonia undergoes fission into 5-*ethoxyhydantoin*-5-*carboxylamide*, which may be also prepared directly from 5-ethoxy-ψ-uric acid by evaporation with aqueous ammonia on a water-bath; it crystallises in needles, m. p. 225° (corr., decomp.). Both 5-ethoxy-4-hydroxy-4 : 5-dihydrouric acid and 5-ethoxyhydantoin-5-carboxylamide are reduced by hydriodic acid to hydantoin.

5-*Methoxy*-1-*methylhydantoin*-5-*carboxylamide*, conveniently prepared from 5-methoxy-1 : 3 : 7-trimethyl-ψ-uric acid by evaporation with ammonia, on reduction with hydriodic acid gives 1-methylhydantoin, and, on oxidation with dichromate and sulphuric acid, methylparabanic acid, $\begin{matrix}CO\cdot NMe\\ | \\ CO\cdot NH\end{matrix}\!\!>\!CO$. 5-*Methoxy*-1 : 3-*dimethylhydantoin*-5-*carboxylamide* crystallises in six-sided tablets, m. p. 201° (corr.), and is obtained by directly methylating 5-methoxy-1-methylhydantoin-5-carboxylamide by means of diazomethane; on reduction by hydriodic acid it yields 1 : 3-dimethylhydantoin. 5-*Methoxy*-1-*methylhydantoin*-5-*carboxymethylamide*, six-sided tablets (from alcohol), which sinter at 185° and melt at 190° (corr., decomp.), and 5-*methoxy*-1-*methylhydantoin*-5-*carboxyethylamide*, prisms, which sinter at 136° and melt at 139° (corr., decomp.), are obtained by evaporating 5-methoxy-1 : 3 : 7-trimethyluric acid on a water-bath with an aqueous solution of the appropriate primary amine.

The paper opens with a summary of the literature relating to derivatives of alloxanic acid. C. K. I.

Preparation of Hydantoins. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 335993; from *Chem. Zentr.*, 1921, iv, 126—127. Compare A., 1919, i, 351, 417).—Ammonia or monoalkylamines are allowed to react with urethanoarylalkylacetic esters of the general formula $CO_2R\cdot NH\cdot CR''R'''\cdot CO_2R'$. Methyl α-amino-α-phenylpropionate by reaction with methyl chloroformate and sodium carbonate solution gives methyl α-urethano-α-phenylpropionate, $CO_2Me\cdot NH\cdot CMePh\cdot CO_2Me$, colourless crystals, m. p. 45°. This when heated for eight to ten hours with alcoholic ammonia gives after removal of alcohol and ammonia, dissolving the residue in dilute sodium hydroxide solution, and acidifying, 5-phenyl-5-methylhydantoin (I), colourless needles, m. p. 193°.

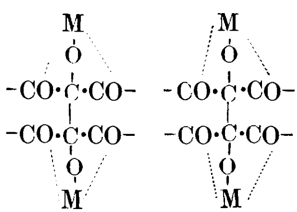
(I.) $CMePh\!<\!\begin{matrix}CO-NH\\ \quad\;\; | \\ NH\cdot CO\end{matrix}$ (II.) $CEtPh\!<\!\begin{matrix}CO-NEt\\ \quad\;\; | \\ NH\cdot CO\end{matrix}$

In a similar manner from ethyl urethano-α-phenylbutyrate, $CO_2Et\cdot NH\cdot CEtPh\cdot CO_2Et$, a thick oil, b. p. 186—188°/21 mm., and alcoholic ammonia, 5-*phenyl*-5-*ethylhydantoin*, is obtained, as colourless spikes, m. p. 197°. By heating the urethano-α-phenylbutyric ester with 35% monoethylamine solution for ten hours, 5-*phenyl*-3 : 5-*diethylhydantoin* (II) is obtained, fine needles, m. p. 88°. By the action of ammonium cyanide on acetopiperone and hydrolysis, α-*amino*-α-*piperonylpropionic* acid is obtained which gives with methyl alcohol and hydrochloric acid the *methyl* ester, a colourless oil, b. p. 193—194°/20 mm., from which by means of methyl chloroformate and sodium carbonate solution *methyl* α-*urethano*-α-*piperonylpropionate* is obtained as colourless crystals, m. p. 78—80°. The latter by heating with alcoholic ammonia gives 5-*piperonyl*-5-*methylhydantoin*, colourless leaflets, m. p. 192—193°. By heating *ethyl* α-*urethano*-α-p-*chlorophenylbutyrate*, a thick oil crystallising after a time in the cold with alcoholic ammonia, 5-p-*chlorophenyl*-5-*ethylhydantoin* is obtained,

colourless needles, m. p. 212°. *p*-Chlorpropiophenone when heated with ammonium cyanide gives *α-amino-α-chlorophenylbutyronitrile*, which by hydrolysis with hydrochloric acid gives *α-amino-α-chlorophenylbutyric acid*. The ethyl ester of the latter gives the corresponding *urethane* by reaction with ethyl chloroformate in the presence of potassium carbonate. G. W. R.

Preparation of Hydantoins. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 335994; from *Chem. Zentr.*, 1921, iv, 126. Compare A., 1919, i, 351, 417).—Alternatively to earlier methods of preparing hydantoins, arylalkylmalononitriles are treated with hypohalogenites. For example, *phenylethylmalononitrile*, b. p. 130—133°/10 mm., prepared from phenylethylcyanoacetamide by distillation in a vacuum with phosphorus pentachloride, gives on treatment with potassium hypobromite solution and subsequent warming *phenylethylhydantoin*. By alkylation of phenylcyanoacetamide, *phenyl*iso*propylcyanoacetamide*, m. p. 127°, is obtained; this gives by distillation with phosphorus pentachloride, *phenyl*iso*propylmalononitrile*, b. p. 143°/13 mm. From the latter *phenyl*iso*propylhydantoin* is prepared, m. p. 210—212°. *Phenylbenzylmalononitrile*, b. p. 194°/11 mm., m. p. 97°, gives similarly *phenylbenzylhydantoin*, m. p. 209—210°. Phenylbenzylmalononitrile is obtained from phenylbenzylacetamide, m. p. 135°. G. W. R.

Tervalent Carbon as Chromophore in the Halochromism of the Alloxantins and Analogous Substances. A. HANTZSCH (*Ber.*, 1921, **54**, [*B*], 1267—1279).—The most remarkable property of alloxantin and of the allied substances, isatide and hydrindantin, is the ability to form violet barium salts. The composition of these has not been fully elucidated previously, and it has been frequently suggested (compare Ruhemann, T., 1911, **99**, 792, 1306) that they are derived from the products of decomposition of these substances. It is now shown, however, that they are really salts of alloxantin, etc., and, under suitable conditions of decomposition, re-form the parent substance. Their constitution naturally depends on that of the parent substances, which has been the subject of much discussion; an exhaustive review of the literature, considered in conjunction with measurements of the absorption spectra, leads the author to prefer the original pinacone-like formulæ containing the groupings $\begin{array}{c}\text{-CO·C(OH)·CO-}\\ \text{-CO·C(OH)·CO-}\end{array}$ or $\begin{array}{c}\text{-CO·C(OH)·}C_6H_4\text{-}\\ \text{-CO·C(OH)·}C_6H_4\text{-}\end{array}$, and to regard these as established when satisfactory explanations can be advanced of the ready rupture of the single carbon bond and the chemical changes during the halochromism. The latter is not sufficiently accounted for by the annexed formulæ, I and II, particularly since Behrend has shown that benzoylalloxantin yields a colourless barium salt. The only possible explanation lies in the assumption of the formation of tervalent carbon as an integral com-



(I.) (II.)

ponent of the chromophoric complex of the violet salts, which thus receive the formula

$$CO<\begin{smallmatrix}NR\cdot CO\\NR\cdot CO\end{smallmatrix}>C\cdot OM \quad C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C\cdot OM \quad NH<\begin{smallmatrix}C_6H_4\\CO-\end{smallmatrix}>C\cdot OM$$

in the three series. They are thus analogous to Schlenk's metallic ketyls. Unfortunately, the unstable nature of the compounds excludes the possibility of the direct measurement of their molecular weight in solution. A difficulty in accepting this interpretation is caused by Ruhemann's observation that hydrindantin dissolves in sodium carbonate with the initial formation of red salts; that the formation of coloured salts from this substance is in reality due to the formation of tervalent carbon is supported by the fact that its solution in pyridine becomes bluish-red when heated to boiling but returns to yellow when cooled. Further, the production of red solutions is not a unique property of aqueous sodium carbonate, but is shown by alkali hydroxide solution when sufficiently dilute, the blue solutions becoming first violet and subsequently red.

[With J. RETINGER and FELIX KRÄMER.]—The barium salt of alloxantin, $C_8H_2O_8N_4Ba_2$, is prepared as a dark-violet, amorphous precipitate when an aqueous solution of alloxantin is treated rapidly with an excess of barium hydroxide solution; it is readily decomposed by water. The violet alkali salts are similarly prepared from alloxantin and alkali alkoxide in absolute alcoholic solution; the *potassium* and *rubidium* compounds are hygroscopic and decompose rapidly. The *sodium* salt, $C_8H_2O_8N_4Na_4$, was analysed. The symmetrical and unsymmetrical dimethylalloxantins give analogous amorphous barium salts, $C_{10}H_6O_8N_4Ba_2$, whilst barium tetramethylalloxantin, $C_{12}H_{12}O_8N_4Ba$, is isolated in the homogeneous condition when very finely divided tetramethylalloxantin is shaken with an excess of aqueous barium hydroxide solution for several hours in the absence of carbon dioxide and oxygen. All these salts re-form the parent alloxantin when added in the freshly-prepared condition to moderately concentrated hydrochloric acid. H. W.

Action of Cyanogen Haloids on Phenylhydrazine. V. Melamine Derivatives. G. PELLIZZARI (*Gazzetta*, 1921, **51**, i, 89—107. Compare A., 1919, i, 134, 201; this vol., i, 363, 403).—With aqueous ammonia (1 mol.) αβ-dicyano-*o*-phenyleneguanidine unites forming a basic compound, similar compounds being obtained with aniline and hydrazine. The properties of these compounds indicate that they are derivatives of melamine, but, since the phenylene group remains linked by one valency to a nitrogen atom of the nucleus, it is evident that they correspond, not with the normal form of melamine, but either with the iminic, or with a mixed form; most probable is the structure $\begin{array}{l}N{=\!=}C\cdot NH{-\!-}C{:}NH\\ |\qquad\ \ |\qquad\quad\ \ |\\ C_6H_4\cdot N\cdot C(NH)\cdot NR\end{array}$.
Melamine itself, when boiled with an acid or base, undergoes gradual hydrolysis to ammeline, melanuric acid, and cyanuric acid, and when boiled with hydrochloric acid, these substituted melamines yield the corresponding ammelines, which retain the iso-structure

$\begin{array}{l} N{=\!=}C\cdot NH\cdot C{:}NH \\ C_6H_4\cdot N\cdot CO\cdot NR \end{array}$. Such ammelines are highly resistant to the action of even concentrated hydrochloric acid, although prolonged boiling with the acid results in complete demolition of the ring, with formation of *o*-phenyleneguanidine, carbon dioxide, ammonia, and amine; possibly, although it was not separated, the corresponding melanuric acid is formed as an intermediate product. With alkali hydroxide the ammelines react more readily, the ring being ruptured, with loss of carbon dioxide and formation of a diguanide; thus, *o*-phenylene*iso*ammeline gives *o*-phenylenediguanide, which, by further action of potassium hydroxide, yields *o*-phenylene-β-guanylcarbamide, this in its turn being hydrolysed to *o*-phenyleneguanidine in presence of mineral acid or alkali. The *o*-phenylene-β-guanylcarbamide thus obtained is identical with that previously prepared by the action of hydrochloric acid on β-cyano-*o*-phenyleneguanidine (A., 1919, i, 134) and since its constitution follows from the known constitution of *o*-phenylenediguanide, the position of the carbonyl group in *o*-phenylene*iso*ammeline is established. If, indeed, the carbonyl occupied the only other possible position, rupture of the ring at that point would result in the formation of an *o*-phenylenediguanide corresponding with the *o*-phenylene-α-guanylcarbamide obtained in another way (A., 1919, i, 201).

The *o*-phenylenediguanide now obtained from *o*-phenylene*iso*melamine was prepared by Ziegelbauer (A., 1897, i, 142) by the direct interaction of *o*-phenylenediamine and dicyanodiamide, this author attributing to it the symmetrical structure

$$C_6H_4{<}{\begin{array}{l}NH\cdot C(NH)\\NH\cdot C(NH)\end{array}}{>}NH.$$

The author's results show that this compound can have only the asymmetric constitution given, so that its direct formation from *o*-phenylenediamine and dicyanodiamide must take place according to the scheme: $C_6H_4(NH_2)_2+CN\cdot NH\cdot C(NH_2){:}NH=NH_3+$ $C_6H_4{<}{\begin{array}{l}-N\\NH\end{array}}{>}C\cdot NH\cdot C(NH_2){:}NH$.

The phenyl-*o*-phenylenediguanide obtained in a similar manner from phenylphenylenemelamine by way of phenylphenylene*iso*ammeline, does not give the corresponding guanylcarbamide when boiled with acid or alkali, but undergoes more profound hydrolysis with formation of phenyleneguanidine, ammonia, aniline, and carbon dioxide: $C_6H_4{<}{\begin{array}{l}-N\\NH\end{array}}{>}C\cdot NH\cdot C(NH)\cdot NHPh+2H_2O=$ $C_6H_4{<}{\begin{array}{l}-N\\NH\end{array}}{>}C\cdot NH_2+CO_2+NH_3+NH_2Ph$; the phenyl-*o*-phenyleneguanylcarbamide may, however, be obtained by the action of nitrous acid on the phenylphenylenediguanide.

With hydrazine, compounds are obtained which correspond with those given by ammonia and aniline; they retain the group $:N\cdot NH_2$, since they yield condensation products with aldehydes.

o-*Phenylene*iso*melamine*, $\begin{array}{l} N{=\!=}C\cdot NH{-\!-}C{:}NH \\ C_6H_4\cdot N\cdot C(NH)\cdot NH \end{array}$, forms a white,

crystalline powder, does not melt at 300°, and exhibits basic properties.

o-*Phenylene*iso*ammeline*, $C_9H_7ON_5$, forms white, crystalline crusts, does not melt at 300°, and exhibits both acid and basic properties; its *hydrochloride* is crystalline, but the *potassium* salt is colloidal and separates in gelatinous form.

o-Phenylenediguanide, $C_8H_9N_5$, forms lustrous, nacreous laminæ, and decomposes at 245°; the nitrate ($+HNO_3$), m. p. 216° (decomp.); *platinichloride*, $(C_8H_9N_5)_2,H_2PtCl_6$; and picrate ($+C_6H_3O_4N_3$), lustrous, yellow needles, m. p. 269—270°, were prepared.

Phenyl-o-*phenylene*iso*melamine*, $\begin{array}{l}N{=\!=}C\cdot NH{-}C{:}NH\\ C_6H_4\cdot N\cdot C(NH)\cdot NPh\end{array}$ $+H_2O$, forms slender, white, lustrous needles, m. p. 241° (decomp.), and gives a *platinichloride*, $(C_{15}H_{12}N_6)_2H_2PtCl_6$.

Phenyl-o-*phenylene*iso*ammeline*, $C_{15}H_{11}ON_5$, crystallises in slender, colourless needles ($+C_2H_6O$), m. p. 292° (decomp.), and exhibits solely basic properties. Its *hydrochloride* and *nitrate*, m. p. 225° (decomp.), and the *picrate* were prepared.

Phenyl-o-*phenylenediguanide*, $C_{14}H_{13}N_5$, crystallises in rounded masses of slender, white needles, m. p. 178°; the *nitrate*, m. p. 173—174° (decomp.) and *platinichloride*, $C_{14}H_{13}N_5,H_2PtCl_6$, were prepared.

Phenyl-o-*phenyleneguanylcarbamide*, $C_6H_4{<}{}^{-N-}_{NH}{>}C\cdot NH\cdot CO\cdot NHPh$, forms crusts of minute crystals and at 250° does not melt but loses aniline with probable formation of a substituted biuret; its *hydrochloride* crystallises in lustrous, pale yellow needles, m. p. 193° (decomp.).

o-*Phenyleneamino*iso*melamine*, $\begin{array}{l}N{=\!=}C\cdot NH{-}C{:}NH\\ C_6H_4\cdot N\cdot C(NH)\cdot N\cdot NH_2\end{array}$, crystallises in long, slender, colourless needles, decomposes at 283°, and exhibits marked basic properties.

o-*Phenyleneamino*iso*ammeline*, $C_9H_8ON_6$, forms microscopic, white needles, m. p. 303°. Its *hydrochloride* crystallises in white needles, which become opaque at about 150°, m. p. 289°; with benzaldehyde it yields *benzylidenephenyleneamino*iso*ammeline*, $\begin{array}{l}N{=\!=}C\cdot NH\cdot C{:}NH\\ C_6H_4\cdot N\cdot CO\cdot N\cdot N{:}CHPh\end{array}$, which forms a felted mass of slender needles, does not melt at 300°, yields benzaldehyde when boiled with dilute acid, and gives a *hydrochloride* with no definite melting point.

o-*Phenyleneaminodiguanide*, $C_8H_{10}N_6$, forms almost colourless crystals, m. p. 195—197° (decomp.), has an alkaline reaction towards litmus and yields a pink compound with a cobalt salt and potassium hydroxide. T. H. P.

Partial Reduction of Nitroazoxybenzenes by means of Hydrogen and Platinum. G. Cusmano and L. Della Nave (*Gazzetta*, 1921, **51**, i, 65—70. Compare A., 1920, i, 298, 886).—When

an ethereal solution of *o*-nitroazoxybenzene (1 mol.), containing platinum-black in suspension, is shaken at the ordinary temperature in an atmosphere of hydrogen (2 mols.), *o*-hydroxylaminoazoxybenzene, *o*-aminoazoxybenzene, *o*-nitroazobenzene, phenylenediamine, and aniline are formed, whilst with 3 mols. of hydrogen, *o*-aminoazoxybenzene, aznitrosobenzene [?], aniline, and *o*-phenylenediamine are obtained. Thus, the reduction follows two directions: either the nitro-group is converted first into a hydroxylamino- and then into an amino-group, the azoxy-group remaining intact, or the azoxy-group is attacked.

o-*Hydroxylaminoazoxybenzene*, $OH{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}NPhO$, crystallises in pale yellow prisms, m. p. 118°, and becomes covered with a red patina when exposed to light. In ethereal solution it is oxidised by freshly-prepared, yellow mercuric oxide to *o*-nitrosoazoxybenzene, whilst catalytic reduction converts it principally into *o*-aminoazoxybenzene, *o*-phenylenediamine also being formed. With phenylcarbimide it gives the *compound* $C_{19}H_{16}O_3N_4$, which forms pale yellow, flattened crystals, m. p. 140° (decomp.).

T. H. P.

Physico-chemical Investigations on Hydroxyazo-compounds. II. E. PUXEDDU and M. GENNARI (*Gazzetta*, 1921, **51**, i, 256—261).—Further measurements of the conductivities of the sodium and potassium salts of hydroxyazo-compounds have been made (compare this vol., i, 366). The purity of the products examined is naturally of great importance, and the most satisfactory method of purification consists in dissolving the hydroxyazo-compound in ammonia solution and reprecipitating it by means of a current of carbon dioxide. The exact neutralisation of a hydroxyazo-compound by alkali hydroxide is important, not only as a means of determining its purity and for the study of the electrical conductivity of its salts, but also since it constitutes a safe criterion for distinguishing between para- and ortho-hydroxyazo-compounds: the former dissolve exactly or almost so in the calculated proportion of alkali hydroxide, whereas the latter dissolve neither in the calculated proportion nor in a considerable excess.

The conductivities of solutions of sodium and potassium salts of *p*-hydroxyazobenzene, benzeneazo-*o*-cresol, and *o*-tolueneazophenol have been measured at 25°. The results differ from those described by Farmer and Hantzsch (A., 1900, i, 122) and show that all the solutions were hydrolysed, although in somewhat varying degree; further, the extent of the hydrolysis does not always increase regularly with the dilution, a definite value of the latter corresponding with a maximal hydrolytic decomposition. The values of $\Delta_{1024-32}$ for the sodium salts of *p*-hydroxyazobenzene, benzeneazo-*o*-cresol, and *o*-tolueneazophenol at 25° are 16·57, 16·97, and 20·27 respectively. The hydrolysis increases with lapse of time owing to the disturbance of the system caused by the separation of the free hydroxyazo-compound, which is only slightly soluble in water.

T. H. P.

Oxidation of *p*-Acetylaminoazobenzene. M. PASSERINI (*Gazzetta*, 1921, **51**, i, 229—232. Compare this vol., i, 197).—It has been shown by Valori (A., 1915, i, 467) that oxidation of *p*-aminoazobenzene in acetic acid solution by means of hydrogen peroxide yields first trisazobenzene, then the compound

$$NPh{:}N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}N{:}NPh,$$

and finally azoxylbisazoxybenzene. It is now found that the acetyl group of *p*-acetylaminoazobenzene protects the amino-group from the oxidising action of peracetic acid, the products formed being the two isomeric *p*-acetylaminoazoxybenzenes; this result confirms Angeli's view of the structure of azoxy-compounds (A., 1913, i, 658). Hydrolysis of the mixed *p*-acetylaminoazoxy-benzenes and re-acetylation of the separated amino-compounds shows that the *p*-aminoazoxybenzenes with m. p. 114° and 134—136° respectively give *p*-acetylaminoazoxybenzenes with m. p. 142—143° and 166° respectively. When the two amino-compounds are treated with peracetic acid, the former yields Angeli's azoxy-bisazoxybenzene, m. p. 230° (*loc. cit.*), and the latter the isomeric azoxybisazoxybenzene, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}N{:}NPh{:}O$, m. p. 223°. Thus the structures of the acetyl- and amino-derivatives from which are derived these polyazoxy-compounds are established.

p-Acetylaminoazobenzene, when crystallised from alcohol, has the constant m. p. 157°, although m. p. 146° is usually attributed to this compound.

p-Acetylaminoazoxybenzene, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NHAc$, forms crystals, m. p. 166°, with slight softening at 160°. The corresponding p-*aminoazoxybenzene*, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NH_2$, crystallises in pale yellow needles, m. p. 134—136°, and the corresponding *azoxy-bisazoxybenzene* (see above), copper-red scales, m. p. 223°.

The isomeric p-*acetylaminoazoxybenzene*, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NHAc$ [? $NPh{:}NO{\cdot}C_6H_4{\cdot}NHAc$], forms colourless crystals, m. p. 142—143°. The corresponding p-*aminoazoxybenzene*, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}NH_2$ [? $NPh{:}NO{\cdot}C_6H_4{\cdot}NH_2$], forms lustrous, yellow plates, m. p. 114°.

T. H. P.

Diazo-derivatives of 4′-Amino-1-phenyl-5-methylbenzothiazole (Dehydrothio-*p*-toluidine). GILBERT T. MORGAN and DOROTHY WEBSTER (T., 1921, **119**, 1070—1077).

Condensation of 2 : 4 : 6-Trinitrophenylhydrazine with Quinones. W. BORSCHE (*Ber.*, 1921, **54**, [*B*], 1287—1290).—It has been shown previously (A., 1908, i, 66) that the quinones of the benzene series react with 2-nitro- or 2 : 4-dinitro-phenyl-hydrazines with the formation of hydroxyazo-compounds, but the method could not then be applied to 2 : 4 : 6-trinitrophenylhydr-azine. This has now been accomplished, the reason of the previous failure appearing to lie in the unexpected instability of the products in alkaline solution.

2 : 4 : 6-*Trinitro-4′-hydroxyazobenzene*, $C_6H_2(NO_2)_3{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$, dark red, lustrous needles, m. p. 194—195°, is prepared by the action of 2 : 4 : 6-trinitrophenylhydrazine on *p*-benzoquinone at the atmospheric temperature and in aqueous alcoholic solution

in the presence of concentrated hydrochloric acid; the corresponding *benzoyl* compound crystallises in long, orange-red needles, m. p. 191°. 2 : 4 : 6-*Trinitro-4′-hydroxy-3′-methylazobenzene* forms garnet-red platelets ($+H_2O$), m. p. 196°. Thymoquinone reacts more slowly with the hydrazine derivatives and the solution on spontaneous evaporation leaves the *substance*, $C_{22}H_{21}O_{13}N_{10}Cl$, orange-red leaflets, m. p. 142—144°, which when recrystallised from dilute acetic acid gives 2 : 4 : 6-*trinitro-4′-hydroxy-2′-methyl-5′-*iso*propylazobenzene*, yellowish-red leaflets, m. p. 162—163°. 4-2′ : 4′ : 6′-*Trinitrobenzene-azo-α-naphthol* forms dark red crystals, m. p. 249° (decomp.), whilst 2 : 2′ : 4′ : 6′-*trinitrobenzeneazo-α-naphthol* crystallises in brown needles, m. p. 230° (decomp.). *p*-Benzoquinoneoxime gradually yields a *compound* of *p*-benzoquinoneoximepicrylhydrazone with picrylhydrazine, decomp. 165—166°, which is converted by boiling glacial acetic acid into *bis-[trinitrobenzeneazo]-azoxybenzene*, decomp. 321°. H. W.

Comparative Investigation of the Corresponding Proteins of Cow and Ox Serum, Cow's Colostrum, and Cow's Milk by the Method of Protein Racemisation. HERBERT ERNEST WOODMAN (*Biochem. J.*, 1921, **15**, 187—201).—The method of Dakin (A., 1913, i, 208, 1249; compare also Dudley and Woodman, A., 1915, i, 468; 1918, i, 178) has been simplified; the course of racemisation under perfectly definite conditions is expressed by a "racemisation curve," and in this way evidence for the identity of euglobulin and pseudo-globulin, whether from serum or colostrum, has been brought forward. The identity of the globulins of cow and ox serum and of colostrum has been confirmed and the albumin of milk and of colostrum are also regarded as identical. Lact-albumin and serum-albumin differ, however. Globulin is a definite chemical individual, the composition of which is unaffected by its mode of preparation (compare also Crowther and Raistrick, A., 1916, i, 864). G. B.

Viscosity of Casein Solutions. HARPER F. ZOLLER (*J. gen. Physiol.*, 1921, **3**, 635—651).—There is a maximum viscosity at P_H 9·1—9·25 in 8—10% solutions containing 98×10^{-5} gram-equivalents of base for 1 gram of casein. With borax, the maximum is at P_H 8·15—8·2; probably casein, like mannitol, increases the dissociation of boric acid. The decrease of viscosity at P_H 10—10·5 and upwards is due to a hydrolysis; the major cleavage product contains no phosphorus or sulphur and less nitrogen than casein. G. B.

Hæmocyanin. C. DHÉRÉ and A. SCHNEIDER (*Compt. rend. soc. biol.*, 1920, **83**, 1505—1507; from *Physiol. Abstr.*, 1921, **6**, 239).—The investigations were made on the blood of crayfish, crab, and cuttle-fish. As in the case of the snail and lobster, complete reduction occurs on aeration with an indifferent gas, also by exhaustion and heating. A green compound was formed with nitric oxide and snail hæmocyanin, but not with lobster hæmocyanin. In the crayfish, the compound is formed in small

quantities by long passage of the gas. Larger quantities are formed in the cuttle-fish. Preparations from snail hæmocyanin gradually assume a yellow colour (compare A., 1920, i, 338).

E. S.

Hæmocyanin. V. Absorption Spectrum of Oxyhæmocyanin in the Ultra-violet. CH. DHÉRÉ (*J. Physiol. Path. gén.*, 1920, **18**, 1081—1093; from *Chem. Zentr.*, 1921, i, 1000. Compare this vol., i, 366).— Hæmocyanin was crystallised from the blood of various crustacea and similar organisms. The absorption spectrum of oxyhæmocyanin showed three lines, namely, λ 278 and 346 in the ultra-violet, the first due to the albumin group of hæmocyanin and the second to a prosthetic copper or pyrrole group, and λ 570 in the visible portion, probably due to copper. The middle line is characteristic.

G. W. R.

Some New Observations in the Study of Bilirubin. W. KÜSTER (*Zeitsch. angew. Chem.*, 1921, **34**, 246—247).—Bilirubin is very conveniently purified through its crystalline ammonium salt, by leading dry ammonia into a suspension of the crude material in boiling methyl alcohol until solution is effected. The filtered solution is evaporated to a small bulk in a stream of hydrogen, and any bilirubin which has separated owing to dissociation is brought into solution again by leading in a further quantity of ammonia. On cooling, the ammonium compound is deposited in crystalline form, and by dissolving in fifteen times its weight of warm pyridine and cooling, bilirubin crystallises out in a pure condition. In spite of the similarity and close relationship between bilirubin and the porphyrins, they differ in their behaviour towards hydrogen bromide and hydrogen iodide in acetic acid solution, bilirubin not giving any basic substance, that is any substance corresponding with hæmatoporphyrin, when the reaction product is poured into water. On the contrary, 3 mols. of hydrogen bromide react, and two bromine atoms only are displaced by the action of water. Hydrolysis with methyl alcohol, however, results in the elimination of 2HBr, whilst the third remains unattacked, and can only be removed by alkali hydroxide. Further, whilst mesoporphyrin in hydrochloric-acetic acid solution is converted by hydrogen peroxide into tetrachloromesoporphyrin, bilirubin is under the same conditions degraded to a dibasic acid termed *hexachlororubilinic acid*, $C_{18}H_{20}O_6N_2Cl_6$, m. p. 160°. Bilirubin can therefore be attacked in two directions: by reduction, when an acidic nucleus remains connected by a CH_2-group with a basic nucleus, and by oxidation, when two acidic nuclei remain in the reaction product and the basic nucleus is destroyed.

G. F. M.

Melanins. ANGELO ANGELI and ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 241—245).—The authors criticise adversely certain of the results and conclusions of Salkowski (A., 1920, i, 572). For instance, although melanin may be destroyed completely by boiling alkaline permanganate solution, with cold 2% permanganate solution containing a few drops of potassium

hydroxide solution it gives, besides oxalic acid, an acid of the pyrrole or indole series. Further, hypomelanin and sepia-black are readily oxidised in the hot by 30% hydrogen peroxide solution diluted with acetic acid giving, on evaporation, a syrupy residue which, when heated either alone or in presence of potassium hydroxide, gives the pine splinter reaction.

Salkowski's observation that the melanins yield pyrrole when fused with potassium hydroxide, the analogies existing between melanins and pyrrole-blacks, the property exhibited by pyrrole of furnishing black or brown products when treated either with ordinary oxidising agents or with oxydases *in vitro* or in living tissue, the fact (compare Saccardi, A., 1920, i, 790) that injections of pyrrole determine in animals, either a melanuria with characters similar to those noted by Eppinger in patients suffering from melanosarcoma or, if following injection of melanin, the formation of melanotic tumours, render it probable that the colour in all these cases is largely due to the one fundamental substance, pyrrole. T. H. P.

The Donnan Equilibrium and the Physical Properties of Proteins. I. Membrane Potential. II. Osmotic Pressure. JACQUES LOEB (*J. Gen. Physiol.*, 1921, **3**, 667—690, 691—714).—Continuing his previous work (this vol., i, 368) the author has measured the potential difference (*P.D.*) which exists at equilibrium between a gelatin chloride solution in a collodion bag and an outside aqueous solution, and shows in several cases that the effect of a neutral salt or of a change of the hydrogen-ion concentration is very similar to the effect on the osmotic pressure, and likewise similar to the effect on the swelling or on the viscosity of the gelatin chloride. The valency of the anion with which the gelatin is in combination also affects these properties similarly, and all these variations like the variation of the *P.D.* may be due to the Donnan effect, which is manifested when a colloid is in solution on one side of a membrane permeable to an acid or base (also present) with which the colloid can form a salt. There results an unequal distribution of the non-colloid ions on the two sides of the membrane (A., 1911, ii, 848).

The *P.D.* may be calculated by Nernst's formula from the value of P_H inside minus P_H outside or from the (equal) expression P_{Cl} outside minus P_{Cl} inside, and the agreement with experiment thus verifies Procter's expression (T., 1914, **105**, 313; 1916, **109**, 307) for the Donnan Equilibrium.

The *P.D.* between solid gelatin and a surrounding aqueous neutral-salt solution varies similarly to its degree of swelling, and can be calculated satisfactorily from the value of P_H inside minus P_H outside.

Assuming Donnan's theory of membrane equilibrium and Procter's equation, $x^2=y(y+z)$, the osmotic pressure of gelatin salts can be calculated, neglecting that part due to the gelatin ions and molecules themselves, and with a varying P_H, the theoretical curves agree qualitatively and to some extent quantitatively with the

experimental—the discrepancies are probably due to the factors omitted in the simplified theory. W. O. K.

Enzymes. VI. Protective Action of Starch and other Substances on Ptyalin in Acid Media. D. MAESTRINI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 315—318. Compare this vol., i, 281).—The author has made experiments with a number of other substances to ascertain if any of them shares with starch the property of protecting saliva from the destructive action of hydrochloric acid. Three classes of substances are distinguished: (1) Egg-albumin dissolved in physiological salt solution and ox-blood fibrin which exhibit no such property. (2) Sweet almond oil, mutton fat, and egg-albumin dissolved in water, which cause the enzymic activity to be far less marked than with 5% starch paste. (3) Animal charcoal which exerts a protective action greatly exceeding that of starch. The action is probably due to simple adsorption of the enzyme. T. H. P.

Sensitiveness of Saccharase towards Ultra-violet Light and towards Oxidising Agents. OLOF SVANBERG (*Arkiv Kem. Min. Geol.*, 1921, **8**, No. 6, 1—17).—The author's experiments show that a saccharase solution with a low proportion of dry matter is more sensitive to the radiation from a mercury lamp than is one with a higher dry matter content, and that the destruction of the enzyme by this means may be prevented by passing hydrogen through the solution while the ultra-violet light is acting on it. From these results the conclusion is drawn that this action of ultra-violet light is mostly a secondary photochemical effect. Agulhon's supposition (A., 1912, i, 61) that the destruction of saccharase in ultra-violet light is to be explained by the formation of hydrogen peroxide is not justified, since the enzyme is highly insensitive towards the peroxide; it is, however, far more sensitive towards ozone, but not sufficiently so to furnish a quantitative explanation of the effect of ultra-violet light.

These oxidising agents exert a far greater effect on amylase solutions and the sensitiveness of this enzyme towards ozone is capable of explaining its destruction by ultra-violet light.

T. H. P.

Synthesising Action of α-Methyl-*d*-mannosidase. H. HÉRISSEY (*Compt. rend.*, 1921, **172**, 1536—1539. Compare this vol., i, 306).—Using lucerne seeds dried and powdered as a source of α-*d*-mannosidase, it has been found possible to synthesise α-methyl-*d*-mannoside from a solution of mannose in 10% aqueous methyl alcohol, but the mannoside was not obtained in quantity sufficient to characterise it other than microscopically. W. G.

Electrical Conductivity of Arsinic Acids. Correction. F. FICHTER (*Ber.*, 1921, **54**, [*B*], 1280).—The conductivities of phenylarsinic, *p*-aminophenylarsinic, and *o*-nitrophenylarsinic acids have been measured by Fichter and Elkind (A., 1916, i, 444) but the results, as far as arsanilic acid is concerned, are not in harmony

with the observations of Lorenz and Schmidt (A., 1920, ii, 465). Revision has disclosed an error in the experiments; the revised figures are now given. H. W.

Derivatives of Sulphur in Commercial Salvarsan. I. HAROLD KING (T., 1921, **119**, 1107—1120).

Action of Mercuric Chloride on Salvarsan and Neosalvarsan. A. BINZ and H. BAUER (*Zeitsch. angew. Chem.*, 1921, **34**, 261—263).—Salvarsan and mercuric chloride form in alcoholic solution an orange-red additive product, but in an aqueous medium this rapidly becomes greenish-black owing to decomposition, which results in the formation of colloidal mercury on the one hand, and oxidation of salvarsan to 3-amino-4-hydroxyphenylarsine oxide, $OH\cdot C_6H_3(NH_2)\cdot AsO$, on the other. The latter substance was identified by passing hydrogen chloride into the solution, when colourless needles of 3-amino-4-hydroxyphenylarsine dichloride hydrochloride were deposited, m. p. 200° (not sharp). The oxidation does not appear to proceed further unless an excess of mercuric chloride is present, in which case the final products are *o*-aminophenol, mercurous chloride, and arsenious acid. The reaction between mercuric chloride and neosalvarsan is more complicated, and of the various possible reactions that which preponderates depends on the relative proportions of the two reagents. Unless mercuric chloride is actually in excess at least six products are formed in greater or lesser amount, according to the conditions, namely: colloidal mercury and neosalvarsanic acid,

$$OH\cdot C_6H_3(NH_2)\cdot As{:}As\cdot C_6H_3(OH)\cdot NH\cdot CH_3\cdot SO_3H,$$

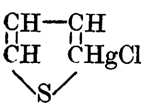
which also remains in colloidal or semi-colloidal solution. These two substances are always formed, and consequently are usually predominating products, and then in addition the following substances may be formed in varying amount: formaldehydesulphurous acid, $OH\cdot CH_2\cdot O\cdot SO_2H$, produced by oxidation of the formaldehyde sulphoxylate residue; 3-amino-4 : 4′-dihydroxyarsenobenzene-3′-iminomethylenesulphurous acid, a bright yellow, insoluble substance produced by oxidation of the neosalvarsan; 3-amino-4-hydroxyphenylarsine oxide, and 4-hydroxyphenyl-arsine-oxide-3-iminomethylenesulphurous acid, both of which remain in solution in the reaction mixture, and may be identified by reduction with hypophosphorous acid to the corresponding arsenobenzene. From a therapeutic point of view, it is pointed out that the arsine oxide products of the decomposition of salvarsan and neosalvarsan, when these substances are used in conjunction with mercuric chloride, are certainly poisonous. G. F. M.

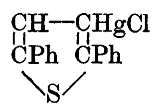
The Action of Magnesium Methyl Iodide on Mercuriated Aromatic Ketones and on Mercuric Chloride. ARTHUR ABELMANN (*Ber. Deut. pharm. Ges.*, 1921, **31**, 240—247. Compare Abelmann, A., 1915, i, 470; Grignard, A., 1916, i, 288).—The action of magnesium methyl iodide on mercuric chloride in ethereal solution at a moderate temperature leads to the formation of

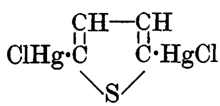
mercuric methyl iodide, lustrous leaflets, m. p. 147°. This compound, together with small amounts of acetophenone and the *substance* $(OH\cdot CMePh\cdot CH_2)_2Hg$, which becomes yellow at 130° and sublimes completely at 150°, is similarly produced from acetophenonemercurichloride, whereas the analogous *substance* $(OH\cdot CMePh\cdot C_6H_4)_2Hg$, m. p. about 130°, after becoming changed at 110°, results from benzophenonemercurichloride. The primary product of the change appears to be the compound $OH\cdot CMePh\cdot CH_2\cdot HgCl$, from two molecules, of which the mercuriated substance described above is obtained by the loss of a molecule of mercuric chloride. The latter is then converted into mercuric methyl iodide. Acetophenone is formed by hydrolysis of the compound $OH\cdot CMePh\cdot CH_2\cdot HgCl$, either directly or after conversion into the corresponding magnesium derivative.

Grignard's method (A., 1916, ii, 149) for the simultaneous estimation of carbon, hydrogen, and mercury does not appear to be applicable to these substances, which must be burnt with lead chromate. H. W.

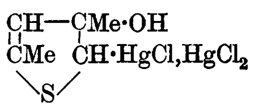
Thiophen–Mercury Compounds. WILHELM STEINKOPF (*Annalen*, 1921, **424**, 23—61).—Further work has not borne out the generalisations previously made (A., 1914, i, 427; 1917, i, 302) regarding the interaction of thiophen derivatives with mercuric chloride, although it remains generally true that thiophens having 2 and 5 positions free form mono- and di-mercurichlorides (types I*a* and II), and that those with but one unsubstituted α-position yield monomercurichlorides (type I*b*) only. This rule is not without exception, however, for 3 : 4-diphenylthiophen shows no tendency to react with mercuric chloride in the cold and on heating it reacts abnormally.

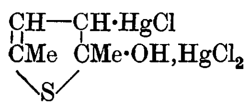

(I*a*.)


(I*b*.)


(II.)

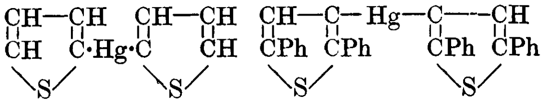
In the next place the formation of stable additive products with mercuric chloride (types III*a* and *b*), which pass with loss of water and mercuric chloride into mercurichlorides of type I only on prolonged boiling with alcohol, is more frequently observed with thiophens containing substituents in both the 2 and 5 positions than when one of these is free. The property, however, is not characteristic of compounds of the former class. 2 : 4-Dimethylthiophen, for example, forms an additive product (III*a*) which is converted on boiling with alcohol into the mercurichloride (type I*a*), whilst 2 : 5-diphenylthiophen yields the mercurichloride (I*b*) without the intermediate formation of any stable additive product.


(III*a*.)


(III*b*.)

Finally, the conversion of mercurichlorides by the action of sodium iodide into mercury dithienyls (type IV*a* and *b*) is not, as was

formerly thought, a characteristic reaction of α-mercurichlorides: 2 : 5-diphenylthiophen-3-mercurichloride (*Ib*) readily yields the mercury dithienyl (IV*b*). Moreover, 2-ethylthiophen-5-mercurichloride (an α-mercurichloride, plainly) does not react with sodium iodide, a circumstance rendered the more remarkable since the known analogues, the mercurichlorides of 2-methyl-, 2-*n*-propyl-, 2-*iso*amyl-, 2-benzyl-, and 2 : 4-dimethyl-thiophens are in every case converted into the corresponding mercury dithienyls under similar experimental conditions.



(IV*a*.) (IV*b*.)

The primary action of sodium thiocyanate on a thiophenmercurichloride results in every case in the formation of the corresponding mercurithiocyanate, and with the mercurichlorides of 2-methyl-, 2-ethyl-, and 3 : 4-dimethyl-thiophens the reaction ceases at this stage, even in the presence of excess of sodium thiocyanate. The mercurithiocyanates of 2-chloro-, 2-bromo-, and 2-iodo-thiophens, of 2 : 4-dimethylthiophen, 2-benzylthiophen, and 2 : 5-diphenylthiophen react further with sodium thiocyanate, however, yielding mercury dithienyls (type IV*a* and *b*) identical with those obtained from the corresponding mercurichlorides by the action of sodium iodide.

The supposed 2 : 4-diphenylthiophen of Baumann and Fromm (*Ber.*, 1897, **30**, 117) yields the same mercury derivatives as 2 : 5-diphenylthiophen and therefore cannot have the constitution previously assigned to it.

The following substances are described for the first time: *thiophen-2-mercurithiocyanate*, glistening leaflets, m. p. 179—180°. 2-*Chlorothiophen*-5-*mercurichloride*, silvery leaflets, m. p. 187°. 2-*Bromothiophen*-5-*mercurichloride*, crystal aggregates, m. p. 187—188°. *Mercury* 5 : 5′-*di-iodo*-2 : 2′-*dithienyl*, m. p. 244—245° (previously obtained in an impure condition). 2-*Iodothiophen*-5-*mercurithiocyanate*, m. p. 173°. *Mercury* 5 : 5′-*dimethyl*-2 : 2′-*dithienyl*, needles, m. p. 162—162·5°; 2-*Methylthiophen*-5-*mercurithiocyanate*, microcrystalline, m. p. 202—204° (decomp.). 2-*Methylthiophen*-5-*mercuribromide*, needles, m. p. 179—180°. 2-*Methylthiophen*-5-*mercuri-iodide*, silvery needles, m. p. 111—112°. 3-*Methylthiophen*-2- (or -5)-*mercurichloride*, m. p. 128—129°. 3-*Methylthiophen*-2- (or -5)-*mercurithiocyanate*, small crystals, m. p. 169° (decomp.). 2-*Ethylthiophen*-5-*mercurichloride*, m. p. 147—148°. 2-*Ethylthiophen*-5-*mercuri-iodide*, silvery needles, m. p. 96—97°. 2-*Ethylthiophen*-5-*mercurithiocyanate*, small leaflets, m. p. 167·5—169°. 2 : 3-*Dimethylthiophen*-5-*mercurichloride*, felted needles, m. p. 213—214°. 2 : 3-*Dimethylthiophen*-5-*mercurithiocyanate*, small felted needles, decomposes on heating. A *substance*, $C_6H_9OSHgCl,HgCl_2$, (from 2 : 4-dimethylthiophen), felted crystals, m. p. 167—168°. 2 : 4-*Dimethylthiophen*-5-*mercurichloride*, m. p. 138—139°. *Mercury* 3 : 5 : 3′ : 5′-*tetramethyl*-2 : 2′-*dithienyl*, silvery leaflets, m. p. 160—161°. 2 : 4-*Dimethylthiophen*-5-*mercuri-iodide*, small glistening crys-

tals, m. p. 137—139°. 2 : 4-*Dimethylthiophen-5-mercurithiocyanate*, m. p. 173—175°. 2 : 5-*Dimethylthiophen-3-mercurithiocyanate*, m. p. 177—177·5°. 3 : 4-*Dimethylthiophen-2-mercurithiocyanate*, m. p. 178—179°. 2-n-*Propylthiophen-5-mercurichloride*, m. p. 155°. 2-n-*Propylthiophen-5-mercurithiocyanate*, silvery leaflets, m. p. 169—169·5°. *Mercury* 5 : 5′-*di*-n-*propyl*-2 : 2′-*dithienyl*, silvery crystals, m. p. 57—58°. 2-iso*Amylthiophen-5-mercurichloride*, felted needles, m. p. 171·5—172°. 2-iso*Amylthiophen-5-mercurithiocyanate*, glistening crystals, m. p. 194—200°. *Mercury* 5 : 5′-*Di*-iso*amyl*-2 : 2′-*dithienyl*, small crystals, m. p. 55—57°. 2-*Benzylthiophen-5-mercurichloride*, m. p. 189—191°. *Mercury* 5 : 5′-*dibenzyl*-2 : 2′-*dithienyl*, m. p. 209—210°. 2 : 5-*Diphenylthiophen-3-mercurichloride*, m. p. 221—222°. *Mercury* 2 : 5 : 2′ : 5′-*Tetraphenyl*-3 : 3′-*dithienyl*, prismatic needles, m. p. 260—261°. 2 : 5-*Diphenylthiophen-3-mercurithiocyanate*, microcrystalline, decomposes on heating. *Ethylmercurithiocyanate*, from sodium thiocyanate and ethylmercurichloride, m. p. 131—131·5°. *Phenylmercurithiocyanate*, from phenylmercurichloride and sodium thiocyanate, leaflets, m. p. 232°. Almost all the above compounds sinter a few degrees below their melting points.

In the original paper full practical details for the estimation of mercury in organic compounds are given. C. K. I.

Physiological Chemistry.

Theory of the Barcroft Differential Blood-gas Apparatus. THOMAS RICHARD PARSONS (*Biochem. J.*, 1921, **15**, 202—208).—Mathematical and experimental (compare Münzer and Neumann, A., 1917, i, 520). G. B.

Absorption Curve of Hæmoglobin and Carbon Dioxide. G. A. BUCKMASTER (*Proc. Physiol. Soc.*, 1920, *J. Physiol.*, 1921, **54**, xcii—xciii; from *Physiol. Abstr.*, 1921, **6**, 195—196).—Solutions of gas-free hæmoglobin (12·8%) were subjected to pressures of carbon dioxide from 0 to 98 mm. at 37°, and found to obey the Dalton–Henry law. They absorb a slightly smaller amount than red blood-cells of the same hæmoglobin content. Large amounts are absorbed between 40 and 60 mm. pressure, and on reduction of pressure the carbon dioxide is rapidly lost. E. S.

A Lecture Experiment on Blood Nitrogen. L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. Chim. Biol.*, 1921, **3**, 174—175).—The behaviour of fishes is compared when placed (1) in a solution of urea (0·5%), (2) in a similar solution to which urease is added, (3) in water plus urease. It is found that they live comfortably in (1) and (3) but die after one hour in (2), when the concentration of ammonia nitrogen is 70 mg. per litre. C. R. H.

Effects of Citrates, Malates, and Phosphates on the Calcium of the Blood. G. W. CLARK (*Proc. Soc. Exp. Biol. Med.*, 1921, **18**, 165—166; from *Physiol. Abstr.*, 1921, **6**, 253).—Repeated subcutaneous injections of citrate, malate, or phosphate, have no effect on the calcium balance of animals receiving a calcium-rich diet. The calcium content of the blood may be temporarily decreased by the injection of large doses of citrate. Animals on a low calcium intake may, after injection of phosphate, show a decrease in the calcium content of the blood and still maintain a positive calcium balance. The suggestion that animals may adjust themselves to different " calcium levels " is emphasised. E. S.

The Chemical and Physiological Investigation of the Fats and Lipoids of the Blood. P. LEMELAND (*Bull. Soc. Chim. Biol.*, 1921, **3**, 134—169).—The existing methods for the estimation of fats and allied substances in the blood are carefully examined and criticised. By modifications and combination of these methods a system of analysis is elaborated, and described in detail, which allows of the separate determination of the total fatty acids, free and combined cholesterol, lipoid phosphorus, and the non-saponifiable matter other than cholesterol. The soaps are also estimated indirectly as fatty acids. C. R. H.

A Crystalline Uric Acid Compound in Ox Blood. A. R. DAVIS and S. R. BENEDICT (*Proc. Amer. Soc. Biol. Chem., J. Biol. Chem.*, 1921, **46**, v—vi; from *Physiol. Abstr.*, 1921, **6**, 188).—The isolation of this compound is described. The analysis indicates that it is composed of uric acid and a pentose combined in molecular proportions. E. S.

Methods of Measuring the Opacity of Liquids. Relation between the Number and Size of Red Corpuscles and the Opacity of their Suspensions. Relation between the Microscopic Appearance of Precipitated Calcium Oxalate and the Opacity of its Suspensions. Opacity of Serum Diluted with Distilled Water, Physiologically Normal Saline, and Ringer's Solution. J. HOLKER (*Biochem. J.*, 1921, **15**, 216—225, 226—231, 232—237, 238—243).—The liquid is slowly run out of a vertical graduated tube until a thin black wire, stretched across the flat bottom on the outside, just becomes visible on looking down the tube through the liquid. An electric lamp is placed in a box vertically beneath the tube, and separated from it by a sheet of opal glass. It is shown experimentally and theoretically that the intensity of the light has little or no influence. Small quantities of fluid are contained in a narrow tube placed between the opal glass and the wider tube; the small tube has a wire below it and readings are taken with a standard suspension in the larger tube and water in the small one, and then with the unknown fluid in the small tube.

Exosmosis and endosmosis in red-blood corpuscles can be detected by the opacimeter and the isotonic point can be determined with accuracy. When the opacity of a suspension of corpuscles

is known, it is possible to calculate their average size from their number, or when the former is known for any given animal, to make the reverse calculation. In physiological and pathological reactions depending on surface, opacity determinations are a more strict measure of the changes taking place than number of particles.

The opacities obtained when potassium oxalate solutions of ncreasing concentrations are mixed with calcium chloride are not proportional to the amounts of calcium oxalate formed. The curve connecting the two is somewhat S-shaped; there is a short, flat piece, representing crystals so small that they tend to redissolve; next comes a steep piece, with the crystals increasing in size to a certain point; beyond that the curve ascends less steeply, the crystals diminish in size but increase in number and begin to form spherical aggregates. Excess of either calcium or oxalate ions decreases the solubility, as is shown by an increase in opacity.

The opacity of serum diluted with distilled water is greater than when it is diluted with 0·85% sodium chloride, and less than when it is diluted with Ringer's solution (containing calcium chloride). The effect depends doubtless on the state of aggregation of the serum globulin. These results are to be applied to such tests as those of Widal and of Wassermann. G. B.

Preparation of Thrombozyme in a State of Purity. P. Nolf (*Compt. rend. soc. biol.*, 1921, **84**, 840—843; *Compt. rend. soc. belge biol.*, 1921, 60—63; from *Physiol. Abstr.*, 1921, **6**, 254).—Tissue extracts contain two substances which influence blood-coagulation —namely, *thrombozyme*, which is specific, and a *thromboplastic substance*, which is not. The preparation of thrombozyme in pure form from horse oxalate plasma is described. It is the substance described by Wooldridge as thrown down from dog's peptone plasma at 0°. The pure substance thus prepared is only capable of reacting with the thrombogen of mammals, and not with that of birds or fish. E. S.

The Compensating Rôle of Chlorides in their Relationships with the Chemical Composition of Humours. W. Mestrezat and (Mlle) S. Ledebt (*Compt. rend.*, 1921, **172**, 1607—1610).—By dialyses of a 0·5% solution of sodium chloride against fresh horse serum until a definite equilibrium was reached and subsequent estimation of the chloride content of the serum and the equilibrated dialysate, the compensating rôle which chlorides can play in the generation, at the expense of blood, of liquids less rich than it in colloids, but in physico-chemical equilibrium with it, is demonstrated. Judging from the figures found for calcium, magnesium, and phosphoric acid in the equilibrated dialysates, chlorine does not appear to be alone as a compensator. W. G.

Hydrogen-ion Concentration in the Contents of the Small Intestine. J. F. McClendon (*Proc. Nat. Acad. Sci.*, 1921, **6**, 690—691).—The author finds, for the contents of the small intestine obtained by the duodenal tube, values of the P_H from 4·7 to 6·2. C. R. H.

Composition of Fatty Tissue under various Physiological and Pathological Conditions. OSKAR SCHIRMER (*Arch. expt. Path. Pharm.*, 1921, **89**, 263—279).—Human fat has usually an iodine number of 65—66·5, corresponding with an olein content of 59·4%, and m. p. 18—20°. The iodine number can be raised or lowered in animal experiments by suet or oil respectively. Fat people have an iodine number of 70—71, thin ones of 60—62. Melting point and iodine number are only parallel in the same species; rabbit's fat has m. p. 40°, yet has the same iodine number as human fat. G. B.

Chemical Modifications of the Vagus Nerve during Digestion. M. LOEPER, R. DEBRAY, and J. TONNET (*Compt. rend. soc. biol.*, 1921, **84**, 819—820; from *Physiol. Abstr.*, 1921, **6**, 247).—The left vagus nerve in dogs alone amongst nerves has a varying sodium chloride content. It is greater during a meal. E. S.

Production of Ammonia in Nerve. S. TASHIRO (*Proc. Amer. J. Physiol.*, 1921, **55**, 281—282; from *Physiol. Abstr.*, 1921, **6**, 181—182).—A basic, volatile substance giving the tests for ammonia is formed in addition to carbon dioxide in nerve during activity. It tends to neutralise the carbon dioxide, although it is not formed in amount sufficient to do so completely, but this may be a factor in the infatigability of nerve. E. S.

The Rôle of Lactic Acid in the Production and Resolution of Muscle Rigor. H. H. WEBER (*Pflüger's Archiv*, 1921, **187**, 165—192; from *Physiol. Abstr.*, 1921, **6**, 180).—The volume changes of minced frog muscle were studied by the use of a specially constructed "osmomoter" closed by a membrane made from ox intestine (permeable to water and salts), and provided with a horizontal graduated capillary for reading volume alterations. Great swelling was produced by 0·02 to 0·05*N*-lactic acid in Ringer's solution, thus supporting von Fürth's theory of the causation of rigor. Heat-coagulated muscle takes up less water from dilute hydrochloric acid than fresh muscle does. The contraction which occurs when acid-swollen muscle is treated with 1% potassium thiocyanate is due to removal of ions, and not to coagulation, which only sets in when the tissue has contracted considerably. That coagulation due to lactic acid is a cause of the resolution of rigor is disproved by the fact that heat coagulation is inhibited by acids, and also that acids inhibit the shrinkage produced by potassium thiocyanate; further, muscle proteins which clot in water remain fluid in presence of 0·02 to 0·05*N*-lactic acid. During the resolution of rigor there is a considerable loss of substance from intact muscles. It is concluded that resolution is due to liquefaction resulting from excessive swelling. E. S.

An Autoxidisable Constituent of the Cell. FREDERICK GOWLAND HOPKINS (*Biochem. J.*, 1921, **15**, 286—305).—De Rey-Pailhade (A., 1888, 1101) showed that extracts of yeast and of many animal tissues reduce sulphur to hydrogen sulphide; he later regarded this action as due to a "hydride of protein" which

he named philothion. The author now shows that it is due to a dipeptide of cysteine and glutamic acid, which may be provisionally named *glutathione*. Heffter, and later Arnold (A., 1911, ii, 306), showed that the nitroprusside reaction of cysteine is given by very many tissues, and by extracts free from protein. Using this reaction as a guide, the author has isolated the new dipeptide from yeast, from muscle, and from mammalian liver. The original must be consulted for details of the complicated method, which depends partly on precipitation of the dipeptide by Hopkins and Cole's acid mercuric sulphate reagent and on the solubility of its phosphotungstate in excess of phosphotungstic acid. The yield is 0·01—0·02% of the fresh tissue employed. The substance was mostly analysed in the oxidised (disulphide) form, $C_{16}H_{26}O_{10}N_4S_2$, which melts at 182—185° and was not obtained crystalline; it is very soluble in water. The reduced thiol form, $C_8H_{14}O_5N_2S$, is, in addition, somewhat soluble in alcohol and has been crystallised. The dipeptide is quite resistant to the action of the proteolytic ferments of the tissues, but is hydrolysed by boiling acids to equimolecular proportions of cystine and glutamic acid. Solutions of the reduced form, shaken with sulphur, give off hydrogen sulphide. The nitroprusside reaction (most sensitive in the presence of ammonia with a high concentration of ammonium salts) is given by proliferating plant tissues, bacteria, and nearly all tissues of vertebrate and invertebrate animals, but not by connective-tissue, nor by blood plasma and serum. In the fowl's egg, the reaction is absent, but is given by a 30-hours' embryo.

The dipeptide glutathione exercises real functions in the chemical dynamics of the cell. In neutral or slightly alkaline solution it is oxidised spontaneously by air to the disulphide and acts as oxygen acceptor; in acid solution it is more stable. The oxidised form, on the other hand, acts as hydrogen acceptor. Fresh tissues, placed in solutions of the oxidised form at 35°, reduce it, as shown by the development of the nitroprusside reaction. Fresh tissues also reduce methylene-blue, but when they have been kept sufficiently long for their reduction potential to have fallen, so that methylene-blue is no longer reduced, they now oxidise the reduced dipeptide under anaerobic conditions; the oxygen for this must therefore come from some other substance. The exact relations depend very greatly on the hydrogen-ion concentration. Thus in slightly acid solutions ($P_H <$ or $= 6·8$) the disulphide form simply competes with methylene-blue for the reducing action of fresh tissues, and as a result, the normal rate of decoloration of the methylene-blue is slowed. In slightly alkaline solutions ($P_H >$ or $=$ 7·4) this rate of decoloration is greatly accelerated by the addition of the oxidised dipeptide, which now functions as a hydrogen acceptor and possesses catalytic properties somewhat resembling those of a co-enzyme. As has been shown by Thunberg, succinic acid and other substances will restore reducing power to washed tissues, but in these substances the hydrogen is attached to carbon and the reaction is irreversible. The relations of the dipeptide to the respiratory substance of Meyerhof (A., 1918, i, 242) have not

been settled, but quantitatively the effect is small compared with that described by Meyerhof. (Compare also Embden, this vol., i, 528.) For reduction ferments compare Bach, A., 1912, ii, 183, for mechanism of oxidative changes, Wieland, A., 1914, i, 1007; also numerous papers by Thunberg [A., 1911, ii, 56, 627; A., 1914, i, 386 (thiol compounds); 1916, i, 627, 863; 1918, i, 140; 1920, i, 784]. G. B.

Effect of Exposure to Low Temperatures on some Physiological, Chemical, and Physical Properties of Amphibian Muscle. DOROTHY LILIAN FOSTER and DOROTHY MARY MOYLE (*Biochem. J.*, 1921, **15**, 334—346).—The osmotic pressure of a muscle rendered non-irritable by keeping at 0° for a week or more, is less than that of a normal muscle. The change in osmotic behaviour may be due to the membrane having become more permeable, or to a diminution in osmotically active particles, as for instance by adsorption. The latter alternative is considered the more likely, since non-irritable muscle recovers to some extent when placed in amphibian Ringer or sodium chloride solutions. G. B.

Composition of Horn and Epidermis. P. G. UNNA (*Med. Klinik*, 1920, **16**, 1276—1277; from *Chem. Zentr.*, 1921, i, 1004).—The epidermis of animals consists of keratin-*A*, which does not give the xanthoprotein reaction and is insoluble in fuming nitric acid, keratin-*B*, which gives a yellow colour and eventually dissolves, keratin-*C*, which gives a yellow colour, but does not dissolve, and horn-albumoses, which dissolve at once with the production of a yellow colour. Keratin-*A* forms the dry external portions of epidermal cells, keratin-*B* and the albumoses the contents of these cells. The epidermis of hairy mammals and birds consists principally of keratin-*C*, together with keratin-*A* and albumoses; that of reptiles contains more keratin-*B*, together with keratin-*A* and albumoses. In the epidermal layer of humans, the horn albumoses preponderate, together with keratin-*A* and -*B*. The keratins confer hardness whilst the albumoses have the contrary effect. In the horns of cattle the ratio of keratin-*B* to albumoses is five times as great as in the epidermis of humans. The latter, although protective, is on account of its composition permeable and reactive. It contains 13% of keratin-*A*, 10% of keratin-*B*, and 77% of albumoses. G. W. R.

Chemical Constitution and Taste of Aldehydes, Ketones, etc. S. FURUKAWA (*J. Tokyo Chem. Soc.*, 1920, **41**, 706—728, 979—980; from *Physiol. Abstr.*, 1921, **6**, 250).—All the experiments were conducted with the nose shut. The results are: (1) Aldehydes and ketones. Anisaldehyde, cinnamaldehyde, heliotropin, salicylaldehyde, *p*-hydroxybenzaldehyde, perillaldehyde, and furfural have a sweet taste. Benzaldehyde (?), vanillin, citral, citronellal, acetaldehyde, formaldehyde, gingerone, menthone, camphor, ionone, methylheptenone, and acetone have not. There is no relationship between the arrangement of chain, open or closed,

and the taste-producing property, although in perfumery the sweet-tasting aldehydes have invariably a cyclic chain, and no ketone has yet been discovered which has a sweet taste. (2) Semicarbazones have a less sweet taste than the aldehydes and ketones. (3) Phenylhydrazones do not have a sweet taste. (4) Oximes. Presence of HC:NOH in a 6-C cyclic ring eliminates the taste. There is no definite correlation between α-oximes and taste. Hydrochlorides of oximes are indifferent. Nitriles of the oximes have a tendency usually to produce a sweeter taste than oximes, but not always. Acetonitriles, amino-oximes, azoximes, and the introduction of acid and amide groups, do not affect the sweet taste. (5) Isomerides. In perfumes having open chains, the sweet taste is common to all isomerides, but not in cyclic compounds. Non-perfumery substances like amino-acids, on the other hand, have an entirely different taste from their optical isomerides. Neither chemical reactivity nor chemical action between taste organs and these compounds is responsible for the sweet taste. A molecule as a whole must play the important part, probably through such medium as molecular vibration, resonance, or electrical vibration. Various reasons are given to show that the factors responsible for taste and odour are not necessarily the same. α-Antiperillaldoxime is not so irritating as anisaldoxime and benzaldoxime, and is not toxic to higher animals. It is the sweetest compound on record, being 2,000 times sweeter than sucrose, and several times sweeter than saccharin. When given to the higher animals, it is eliminated as gluconic acid. The taste and relative sweetness of perillaldehyde and its derivatives is mentioned. In the second paper the author reports that acetophenoneoxime tastes sweet, and so his statement that no oximes of ketones in perfumery are known to have a sweet taste is corrected. E. S.

Physiology of the Silkworm. ALEXANDER PRINGLE JAMESON and WILLIAM RINGROSE GELSTON ATKINS (*Biochem. J.*, 1921, **15**, 209—212).—The blood of *Bombyx mori* has P_H 6·8 and that of the silk gland is very similar. The digestive secretion has P_H 9·0—9·8; the hind-gut is less alkaline (P_H 8·4). The gut of the moth is acid (P_H 5·2—5·8). The digestive juice has a peculiar diastase, active in strongly alkaline solution; also a maltase. A feeble maltase and more active invertase are present in the blood or hæmocœlic fluid. Catalase is present in both the blood and the digestive juice; oxydases are absent. (Compare Kawase, Suda, and Saitô, this vol., i, 379, 381.) G. B.

The Distribution of Saline Substances and Mineral Elements in Milk. CH. PORCHER and A. CHEVALLIER (*Compt. rend.*, 1921, **172**, 1605—1607).—The authors have prepared an artificial milk in which all the chemical and physico-chemical relations of the components of the milk correspond with an average milk. This is only an approximation but from it they arrive at the following distribution of the mineral ingredients of milk in grams per litre. Sodium chloride, 1·09; potassium chloride, 0·92; calcium citrate, 1·78; magnesium citrate, 0·76; potassium citrate, 0·67; sodium

hydrogen carbonate, 0·25; monopotassium phosphate, 1·0; dipotassium phosphate, 1·10; dicalcium phosphate, 1·06; dimagnesium phosphate, 0·16; potassium sulphate, 0·18; and calcium caseinate, 0·61. W. G.

The Cholesterol Content of Human and Cow's Milk. L. Wacker and K. F. Beck (*Zeitsch. Kinderheilk.*, 1921, **27**, 288—292; from *Physiol. Abstr.*, 1921, **6**, 216).—The amount of cholesterol in human milk depends on the duration of lactation and also shows individual fluctuations. The average values are: human milk, 3·29% fat, 0·1385% cholesterol; cow's milk, 3·65% fat, 0·1258% cholesterol. The cholesterol is in the form of cholesterol esters. Besides the cholesterol and milk fat, a substance soluble in alcohol and ether, and unsaponifiable, is also present. E. S.

Influence of the Nervous System on the Excretion of Creatinine. Experiments on Nervous and Mental Patients. Abraham Albert Weinberg (*Biochem. J.*, 1921, **15**, 306—311).—Muscular tonus is not the preponderating factor in the excretion of creatinine; an important influence should be assigned to the mind. G. B.

Composition of the Unsaponifiable Matter of the Ether Extract of Human Fæces. John Addyman Gardner (*Biochem. J.*, 1921, **15**, 244—273).—Cholesterol, coprosterol, and ψ-coprosterol can all be distilled unchanged at about 220°/1 mm., and also by superheated steam. The unsaponifiable part of the ether extract from more than 50 kilos. of mixed human fæces was partly crystallised from acetone, and the dark oil left after removing the bulk of the crystalline sterols was distilled with superheated steam, and then fractionally at 1 mm., and yielded cholesterol, β-cholestanol, cetyl alcohol, a higher alcohol, and an ill-defined oil of high boiling point, suggesting that there is an unknown substance accompanying the known sterols. The opinion of Lifschütz (compare, for instance, A., 1914, i, 683) that cholesterol is first oxidised in the blood to oxycholesterol, is criticised. G. B.

β-Oxidation and Paired Linkings. K. Spiro (*Helv. Chim. Acta*, 1921, **4**, 459—472).—A theoretical discussion in which new experimental evidence is not adduced.

The different course of oxidation suffered by acids with an even and uneven number of carbon atoms within the organism is also shown in certain purely chemical observations and is paralleled by certain other physiological effects such as taste and smell (phenylbutyl and phenylhexyl alcohols have a slightly unpleasant odour, whereas phenylamyl and phenylheptyl alcohols have pleasant odours of lemons and roses respectively). Examination of purely physical constants, for example, melting points of the fatty acids or hydrocarbons, shows that the substances with odd and even numbers of carbon atoms respectively form two independent series. This parallelism between melting point (as characteristic of structure) and physiological behaviour extends even to details. The melting points of the first members of both series are not typical

and do not conform to rule, the typical series commencing with the fourth or fifth member. The same is true of physiological behaviour; formic and acetic acids behave peculiarly in the organism whilst propionic acid is oxidised to α- and not to β-hydroxypropionic acid. A general characteristic of the aliphatic series is obviously involved which, however, may be masked by the presence of certain groups, for example, $-NH_2$. The regularities in homologous series (oscillation) cannot be recognised in the same manner with substituted or branched chains and, in these cases also, β-oxidation is not observed in the organism. They are more frequently and more sharply observed with solid than with vaporised substances, which is explained by the effect of rise in temperature causing the loosening of intramolecular linkings; thus β-oxidation occurs at relatively low temperatures both within and without the organism whilst, at higher temperatures, α-oxidation occurs.

The widespread occurrence of paired linkings is further illustrated by von Weimarn's theory of colloids and by Karrer's recent work (this vol., i, 310, 313) on the structure of the higher carbohydrates.

H. W.

The Mode of Action of 4-β-Aminoethylglyoxaline (Histamine) on the Human Organism. P. SCHENK (*Arch. Expt. Path. Pharm.*, 1921, **89**, 332—339).—All the effects produced by subcutaneous injections of 4-β-aminoethylglyoxaline are suppressed by simultaneous injection of one-tenth the amount of adrenaline. 4-β-Aminoethylglyoxaline has no effect on the sugar tolerance either normally or after adrenaline; its general effect is to paralyse the sympathetic nervous system.

C. R. H.

Phagocytosis of Solid Particles. III. Carbon and Quartz. WALLACE O. FENN (*J. gen. Physiol.*, 1921, **3**, 575—593).—Silicious dust, inhaled, remains in the lungs and causes phthisis (in gold mines); coal dust moves out and is harmless. This is apparently a surface tension effect. Rhumbler has shown that when coal and quartz particles are rubbed up in oil and sprayed into 70% alcohol the coal remains inside the oil drops and the quartz collects on their surface. Similar principles are used in the flotation process for separating ores.

Carbon particles, suspended in serum, are ingested by leucocytes about four times as fast as quartz particles, and by sponge-cells three times as fast. This is probably connected with the greater stability of carbon suspensions. Opsonins and agglutinins seem to increase phagocytosis through a clumping of the bacteria by the immune serum, and this again may be due to a change of surface tension, which makes them more readily ingested by the leucocytes.

G. B.

Trinitrotoluene Poisoning. L. LEWIN (*Arch. exp. Path. Pharm.*, 1921, **89**, 340—359).—Clinical and animal observations, some pre-war, which do not greatly advance our knowledge of the mechanism of the poisoning (compare, however, Lipschitz, this vol., i, 203).

G. B.

Present State of the Nucleic Acid Question. HENRI MOREL (*Bull. Soc. Chim. Biol.*, 1921, **3**, 176—194).—Useful review; the author promises an account of his own work on the hydrolysis of nucleic acid by snake venom. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Proteolytic Activity of Lactic Organisms. V. Phenomena of Sudden Physiological Mutation. CONSTANTINO GORINI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 312—315).—The author's observations indicate that lactic acid organisms are capable of exhibiting sudden and spontaneous mutation and retro-mutation in their acidifying and proteolytic activity; the new properties acquired in this way are transmissible independently of the conditions of development. These phenomena do not, however, apply to a culture as a whole, but only to certain fractions of it, so that they may be regarded as resulting from simple variations related to inevitable individual divergences of the bacterial cells of one and the same species. Thus, such mutations are not abnormal but rest on fortuitous seeding composed exclusively, or almost so, of cells of one type. T. H. P.

Influences of Reaction on Colour Changes in Tryptophan Solutions. ELFRIDA CONSTANCE VICTORIA MATTICK and ROBERT STENHOUSE WILLIAMS (*Biochem. J.*, 1921, **15**, 213—215).—Tryptophan is coloured yellow to orange by *Bacillus proteus vulgaris* only at P_H 8·9—9·4. The practical bearing of this is concerned with the manufacture of Stilton cheese (compare Cornish and Williams, A., 1917, i, 613; Venn, A., 1920, i, 461). G. B.

Oxidation of Glycerol by *Bacillus subtilis*. E. AUBEL (*Compt. rend. Soc. Biol.*, 1921, **84**, 574—576; from *Chem. Zentr.*, 1921, iii, 50. Compare A., 1920, i, 700).—Ten-day cultures of *Bacillus subtilis* in nutrient solutions containing glycerol were extracted with ether and the residue was treated with sodium hydrogen sulphite. The hydrogen sulphite compound was decomposed by sulphuric acid, dissolved in ether, and again evaporated. The residue was dissolved in water and kept for twenty-four hours at the ordinary temperature after addition of phenylhydrazine and lactic acid. A red *substance*, m. p. 190°, believed to be the phenylhydrazone of pyruvic acid, was obtained. With the distillate from the culture solution, an *osazone* of m. p. 240° was obtained, which had the characters of the osazone of acetyl methylcarbinol. In the residue from distillation, traces are found of a substance optically inactive but reducing Fehling's solution weakly. After addition of sulphuric acid, a distillate is obtained which gives with codeine the coloration characteristic for methyl

glyoxal. The substance is therefore probably dihydroxyacetone. Pyruvic acid plays an important part in biological syntheses. Cultures develop better in media containing pyruvic acid than in those containing dextrose. The successive steps in the oxidation of glycerol are probably glycerol $\rightarrow$ dihydroxyacetone $\rightarrow$ methylglyoxal $\rightarrow$ pyruvic acid. G. W. R

Influence of the Nitrogenous Material Elaborated by *Azotobacter* on the Alcoholic Ferment. E. Kayser (*Compt. rend.*, 1921, **172**, 1539—1541).—The addition of an *Azotobacter* culture, even in small amount, to an alcoholic fermentation injures, as a rule, the multiplication of the yeast, increases the decomposition of the sugar, and may stimulate the zymase action and increase the yield of alcohol. The type of yeast, the age of the bacterial culture, and the manner in which it is used are important factors in determining the result. W. G.

Adaptation of a Yeast to Galactose. Hans von Euler and Ingvar Laurin (*Arkiv Kem. Min. Geol.*, 1920, **7**, No. 28, 1—11).—The circumstances attending the increase in the velocity of fermentation produced by yeast water (Euler and Johannson, A., 1912, ii, 590, and others) render it probable that Harden's co-enzyme, by furthering the growth and increase of the yeast, exerts a marked influence on adaptation phenomena. The authors find that extraction of carefully dried yeast leads to a condition of the cells in which these exhibit fermenting power far exceeding that of fermentation by zymase and yet cease to grow. This result indicates that, by suitable treatment, a growth activator may be withdrawn from yeast, whilst the fermentation activator still remains in the cells in sufficient quantity. T. H. P.

The Salt Effect in Alcoholic Fermentation. Arthur Harden and Francis Robert Henley (*Biochem. J.*, 1921, **15**, 312—318. Compare A., 1920, i, 914, and this vol., i, 480).—The authors have confirmed the observation of Meyerhof (A., 1919, i, 57) that the chlorides, and particularly the sulphates, of sodium and potassium depress the fermentation of dextrose and lævulose by yeast juice or zymin in the presence of phosphates. Salts diminish the rate of action of hexose phosphatase, but have no effect on carboxylase. The depressing effect of potassium sulphate is not affected by acetaldehyde, and thus differs from the depression due to excess of phosphate, which latter effect is greatly diminished by the aldehyde. G. B.

An Abnormal Permeability [of Epidermal Cells] for Urea Solutions. K. Höfler and A. Stiegler (*Ber. Deut. bot. Ges.*, 1921, **39**, 157—164. Compare Höfler, A., 1918, i, 383).—The authors have studied the permeability of the epidermal cells of *Gentiana Sturmiana*, Kern., for urea by means of observations on the volume changes of protoplasts in sections immersed in urea solutions. The values obtained are many times greater than the corresponding values for other plants. The exceptional behaviour of *Gentiana* is also shown in the ratio, permeability for urea : per-

meability for potassium nitrate. The epidermal cells show a much higher permeability for urea than the ground tissue, a fact which has also been observed in the case of certain other plants.

G. W. R.

The Physiological Rôle of the Anthocyanins. STAN JONESCO (*Compt. rend.*, 1921, **172**, 1311—1313).—In wheat and buckwheat plants in which anthocyanin pigments had formed in sunlight, the amount of anthocyanin and flavone glucosides diminished steadily when the plants were kept in the dark. The non-reducing sugars and starch also diminished in amount, but the cellulose increased. The reducing sugars increased in the case of wheat, but decreased in that of buckwheat. W. G.

Occurrence of Thiocyanic Acid in Plants. S. DEZANI (*Staz. sperim. agrar. ital.*, 1920, **53**, 438—450; from *Chem. Zentr.*, 1921, i, 814).—Thiocyanic acid was absent from extracts of the bulbs of *Allium cepa*, the seeds of *Phaseolus vulgaris* and *Pisum sativum*, wheat flour, carrots, apples, chicory, endive (leaves), and spinach. Positive reactions were, however, obtained in extracts of the roots of *Brassica rapa*, *Cochlearia armoracia* and *Raphanus sativus*, in the fresh leaves of *Raphanus raphanistrum*, *Thlaspi bursa pastoris*, *Calepina corvini*, *Sisymbrium alliaria*, *Sisymbrium officinale*, *Nasturtium officinale*, *Bunias erucago*, *Eruca sativa*, *Sinapis alba*, *S. nigra*, and *S. arvensis*. Positive reactions in the case of hay are probably due to the presence of cruciferous plants. The thiocyanic acid where found is probably present as such and is not a decomposition product of allylthiocarbimide. G. W. R.

Presence of Calcium Thiosulphate in *Achromatium oxaliferum*, Schew. GERMAINE HANNEVART (*Bull. Acad. Roy. Belg.*, 1920, 600—605; from *Chem. Zentr.*, 1921, i, 842—843).—In the vacuoles of *Achromatium oxaliferum*, Schew., sulphur granules occur accompanied by another substance which proves to be calcium thiosulphate. The vacuolar substance disappears at 50—60° and sulphur separates. In pure water, the bacteria quickly lose all sulphur by change to hydrogen sulphide. G. W. R.

The Carbohydrate Content of the Navy Bean. W. H. PETERSON and HELEN CHURCHILL (*J. Amer. Chem. Soc.*, 1921, **43**, 1180—1185).—The largest portion of the nitrogen-free extractives of navy beans, Alaska garden peas, and Canadian field peas consists of starch. In a 1917 sample of navy beans, of the 58·97% of nitrogen-free extractives 35·20% was starch and 8·37% was pentosans. In a 1919 sample, of the 61·80% of nitrogen-free extractives 50·54% was total reducing substances calculated as starch. In Alaska garden peas, the nitrogen-free extractives were 60·26% and starch 51·21%, and in Canadian field peas, the nitrogen-free extractives were 54·47% and starch 45·11%. The completeness of digestion of legumes by malt diastase is greatly enhanced by grinding. The amount of starch obtained from a ten hours' digestion was but little greater than that found with four hours' digestion. W. G.

Chemical Constituents of Green Plants. XII. Volatile Constituents of Oak Leaves. HARTWIG FRANZEN (*Zeitsch. physiol. Chem.*, 1921, **112**, 301—316).—The leaves of *Quercus sessiliflora* contain minute quantities of methyl alcohol, hexenol, and lower homologues, and higher unsaturated alcohols. Unsaturated alcohols have been found in some forty plants and hexenol seems to be a constant constituent. Oak leaves also contain formic, acetic, and higher unsaturated acids, acraldehyde, butaldehyde, valeraldehyde, hexaldehyde and higher aldehydes and Δ^{α}-hexenaldehyde (compare A., 1912, ii, 797, 978, 979).

G. B.

Nitrogen Distribution of the Proteins Extracted by Dilute Alkali from Pecans, Peanuts, Kafir, and Lucerne. C. T. DOWELL and PAUL MENAUL (*J. Biol. Chem.*, 1921, **46**, 437—441).—The proteins were extracted by dilute alkali (sodium or barium hydroxide) and precipitated by acidification with acetic acid. The nitrogen distribution was then determined by van Slyke's method. Tables of results are given. From the data obtained it is suggested that extraction of proteins by alkalis prior to analysis by van Slyke's method may be generally applicable when it is desired to obtain the amino-acid composition of foods rather than to isolate individual proteins. E. S.

Amylases of the Cereal Grains—Rye. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (Trans., 1921, **119**, 805—809).

Acid Soil Studies. I. A Study of the Basic Exchange between Soil Separates [Mechanical Fractions] and Salt Solutions. R. H. ROBINSON (*Soil Sci.*, 1921, **11**, 353—362).—The behaviour of the various fractions, separated from four different soils by mechanical analysis, when treated with several different salt solutions, was examined. For a given soil the different fractions liberated approximately the same amount of acid when treated with the same salt solution, but the mode of action of salts of mineral acids was different from that of salts of organic acids. The acidity by treatment with salts of mineral acids was due mainly to aluminium and iron salts rendered soluble by base exchange, but in the case of salts of organic acids it was due to the actual liberation of the organic acid. W. G.

Acid Soil Studies. II. Changes in Calcium Compounds added to Acid Soils. R. H. ROBINSON and D. E. BULLIS (*Soil Sci.*, 1921, **11**, 363—367).—When calcium carbonate or oxide was added to several acid soils and the soil exposed to the weather for one year, it was found that the calcium was retained for the most part as humate or easily decomposable silicate. An exception was with an acid soil, which, according to field observations, did not respond to lime, and in this case the added calcium was combined chiefly as easily decomposable silicate. W. G.

Organic Chemistry.

A New Process for Preparing Sodium Derivatives of True Acetylenic Hydrocarbons. PICON (*Compt. rend.*, 1921, **173**, 155—158).—True acetylenic hydrocarbons react with sodamide in liquid ammonia to give quantitative yields of their sodium derivatives. The higher members from *iso*heptinene upwards react with sodamide in boiling benzene solution.

If sodium acetylide is heated at 180—210° in a vacuum, pure sodium carbide is obtained. If the carbide is heated at 290°, it is decomposed into sodium and carbon. W. G.

Preparation of Chloro- and Bromo-trinitromethane. ERICH SCHMIDT, RICHARD SCHUMACHER, and HANS KUHLMANN (*Ber.*, 1921, **54**, [*B*], 1483—1484).—The substances are prepared by the gradual addition of the halogen to a well-stirred, ice-cold suspension of potassium nitroform in ether. *Chlorotrinitromethane* is a colourless liquid, b. p. 32°/10 mm., m. p. + 4·5°, which liberates iodine from potassium iodide, and is rather more stable towards alkali than is the corresponding bromo-compound; bromotrinitromethane has b. p. 55—56°/12 mm., m. p. + 17 to + 18°. Potassium nitroform is prepared by the gradual addition of a solution of potassium ethoxide to an ice-cold solution of nitroform in alcohol; the product is filtered and washed with alcohol and ether. H. W.

The Preparation of some Allyl Compounds. SAMUEL COFFEY and CHARLES FREDERICK WARD (T., 1921, **119**, 1301—1306).

Action of Heat on Allyl Alcohol in the Presence of Different Catalysts. PAUL SABATIER and BONASUKE KUBOTA (*Compt. rend.*, 1921, **173**, 17—22).—A general consideration of the behaviour of allyl alcohol when passed over metallic oxides at 350°. There are two principal types of reaction. Manganous oxide or finely divided copper produces almost exclusively dehydrogenation into aldehydes; tungsten, thorium, or aluminium oxides cause dehydration with production of hydrocarbons, whilst zirconium or uranium oxides favour both types of reaction. Certain secondary reactions may occur with the production of propaldehyde, propylene, acraldehyde, and more complex condensation products. W. G.

Catalytic Decomposition of Allyl Alcohol. Special Action of Different Oxides. PAUL SABATIER and BONASUKE KUBOTA (*Compt. rend.*, 1921, **173**, 212—216).—An elaboration of work previously published (preceding abstract), in which a detailed account of the reactions occurring in the presence of various metallic oxides is given. Tungsten oxide was found to be the most active of all the catalysts examined. W. G.

A New Method for Determining the Relative Position of the Hydroxyl Groups in the Saturated Glycols. J. BÖESEKEN and P. H. HERMANS (*Rec. trav. chim.*, 1921, **40**, 525—528).—The method is based on the determination of the equilibrium constants in the equation, glycol + acetone $\rightleftharpoons$ dioxymethylene derivative + water. A known weight of the glycol is mixed with a known weight of acetone, one drop of strong sulphuric acid is added, and the mixture kept for twelve hours at 18°. At the end of this time a sufficient excess of dilute aqueous potassium hydroxide is added and the free acetone estimated iodometrically. W. G.

Linolenic and Hexabromostearic Acids and some of their Derivatives. SAMUEL COFFEY (T., 1921, **119**, 1306—1310).

Hydrogenation of some Marine Animal Oils. H. MARCELET (*Compt. rend.*, 1921, **173**, 104—107).—The oils examined were hydrogenated by passing hydrogen at the ordinary pressure through the oil containing 2% of basic nickel carbonate at 250°. All the oils lost their disagreeable odour in the first hour, and the iodine value dropped first rapidly and then slowly as the hydrogenation proceeded further. In all cases, the percentage lowering of the iodine value at the stage when the oil began to solidify at the ordinary temperature was about 40—50%. W. G.

The Condensation of Chloroacetic Ester with Magnesium in the Presence of Ethyl Acetate. MARCEL SOMMELET and J. F. HAMEL (*Bull. Soc. chim.*, 1921, [iv], **29**, 545—553).—In the formation of ethyl acetoacetate by the action of magnesium on ethyl chloroacetate in the presence of ethyl acetate, the ethyl acetate apparently condenses with the magnesium derivative of ethyl chloroacetate which is first formed. Benzoyl chloride reacts with the products of condensation to give a mixture of ethyl benzoylacetate and ethyl α-benzoylacetoacetate as indicated by the preparation of their copper derivatives. If in the condensation the ethyl acetate is replaced by ethyl *iso*valerate a small amount of a β-*ketonic ester*, b. p. 104—106°/12 mm., giving a *copper* derivative, m. p. 150°, is obtained and is possibly ethyl *iso*valerylacetate. W. G.

Condensation of Esters with the Esters of α-Bromo-acids in the Presence of Zinc. Ethyl γ-Ethoxyacetoacetate. MARCEL SOMMELET (*Bull. Soc. chim.*, 1921, [iv], **29**, 553—565).—A more detailed account of work already published (A., 1907, i, 107; 1911, i, 109; 1912, i, 334). W. G.

Cupritartrates. JOHN PACKER and IAN WILLIAM WARK (T., 1921, **119**, 1348—1355).

Experiments on the Synthesis of the Polyacetic Acids of Methane. II. Some Abnormal Condensations of Malonic and Cyanoacetic Esters with Halogenated Methanes. CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL (T., 1921, **119**, 1222—1231).

The Action of Unimolecular Formaldehyde on Grignard's Compounds. ERICH KRAUSE (*Ber.*, 1921, **54**, [*B*], 1466).—In connexion with Ziegler's recent communication on this subject (this vol., i, 394), it is pointed out that the author has previously described the use of unimolecular formaldehyde for the lengthening of carbon chains (Grüttner and Krause, A., 1917, i, 123). H. W.

Preparation of Acyclic δ-Diketones. E. E. BLAISE (*Compt. rend.*, 1921, **173**, 313—315).—Magnesium ethyl bromide condenses with glutaronitrile to give a very small yield of *αγ-dipropionylpropane*, $CH_2(CH_2{\cdot}COEt)_2$, m. p. 58°; b. p. 124—125°/19 mm., giving a *disemicarbazone*, m. p. 195—196°. Other products of the condensation are a nitrogenous *compound*, giving a semicarbazone, and a resinous material, which when warmed with strong hydrochloric acid gives a basic *compound*, m. p. 57°; b. p. 120—125°/13—14 mm. If the glutaronitrile is replaced by glutaro-bis-diethylamide, a much bigger yield of αγ-dipropionylpropane is obtained. *αγ-Dibutyrylpropane*, $CH_2(CH_2{\cdot}COPr)_2$, m. p. 55°; b. p. 150—154°/25 mm., giving a *disemicarbazone*, m. p. 173°, was similarly prepared. These δ-diketones readily undergo cyclisation in the presence of acids or alkalis, and in this way dipropionylpropane yields 1-*methyl*-2-*ethyl*-6-cyclo*hexenone*, b. p. 105°/19 mm., giving a *semicarbazone*, m. p. 250°. W. G.

Preparation of Galactose. E. P. CLARK (*J. Biol. Chem.*, 1921, **47**, 1—2).—A solution of lactose in two and a half times its weight of 2% sulphuric acid is boiled for two hours, then neutralised with barium carbonate, and the solution decanted through a layer of active carbon. The filtrate is concentrated under diminished pressure until its weight is 1·1 times that of the lactose taken. Galactose slowly crystallises on addition of ethyl and methyl alcohols to the warm syrup and seeding. The crude product is purified by adding a few c.c. of glacial acetic acid to a 25% aqueous solution, concentrating and then saturating with 95% alcohol. E. S.

The Polymerisation of Glucosans. AMÉ PICTET and JAQUES PICTET (*Compt. rend.*, 1921, **173**, 158—160).—When glucosan is heated with zinc chloride at 135° under a pressure of 15 mm., it yields *diglucosan*, m. p. 150° (decomp.), but if the heating is carried out at the ordinary pressure the product is *tetraglucosan*. These two polymerides do not react with phenylhydrazine or with magenta decolorised by sulphurous acid, and are only very feeble reducing agents. When heated with zinc chloride at 155° in an open vessel, lævoglucosan gives tetralævoglucosan. These polymerides are readily hydrolysed by dilute acids to dextrose, and there is some indication that with weak acids disaccharides are formed as intermediate products. W. G.

Chemistry of Diastase. I. Constitution of Maltose from the Point of View of the Chemical Dynamics of its Hydrolysis. EIICHI YAMAZAKI and NOBUO YAMADA (*J. Tokyo Chem. Soc.*, 1920, **41**, 621—690).—The concentrations of the products of hydrolysis

of maltose by maltase have been calculated and experimentally determined under various conditions. The author considers that the stable form of maltose in water may be represented by the formula,

$$HO\cdot \underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot$$
$$CH_2\cdot O\cdot \underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH,$$

whereas the solid form possesses the formula,

$$\underbrace{CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot$$
$$CH_2\cdot O\cdot \underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH.$$

Analogous consideration of the behaviour of sucrose indicates that Haworth's formula is more probably correct than that of Fischer.

CHEMICAL ABSTRACTS.

Unsaturated Reduction Products of the Sugars and their Transformations. II. New Anhydro-sugars. Synthesis of a Glucosidomannose. Structure of Cellobiose. MAX BERGMANN and HERBERT SCHOTTE (*Ber.*, 1921, **54**, [*B*], 1564—1574).—It has been shown previously (this vol., i, 307) that glucal is oxidised by perbenzoic acid to mannose and that anhydromannose is intermediately formed. The constitution of the latter substance, $O<\begin{matrix}CH\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH_2\cdot OH\\ \underbrace{CH\text{---}O}\end{matrix}$, is elucidated from the observation that it is converted by water and alcohol into mannose and an alkylmannoside respectively. Similar results are obtained with rhamnal and cellobial. A new method of preparing glucosides is thereby indicated which, in so far as it has been examined, has yielded only α-forms. It is remarkable that the new anhydrides are much less stable towards water and alcohol than is glucosan, although similar ethylene oxide and furan rings are present in each.

Confirmation of the constitution assigned by Haworth and Leitch (T., 1919, **115**, 709) to cellobiose is obtained by the following line of reasoning, which brings additional evidence that the second sugar residue is attached to the oxygen atom of carbon 5. Two hydroxy-groups are replaced by a double bond during the conversion of cellobiose to cellobial. If, now, two hydrogen atoms are added and the compound is hydrolysed by emulsin, the same hydroglucal is obtained as is derived by the direct reduction of glucal. Further, the furan ring in cellobial connects the carbon atoms 1 and 4 so that it is impossible for the sugar residue to be attached to the carbon atoms, 1, 2, or 4 [the latter point of attachment has been advocated by Wrede (this vol., i, 161)]. Further evidence in this connexion is promised in a subsequent communication.

α-Methylmannoside, m. p. 191—192°, $[\alpha]_D$ +79·0° in aqueous solution, is prepared by the oxidation of glucal with a solution of

perbenzoic acid in anhydrous ethyl acetate and treatment of the product with cold methyl alcohol. Similarly, rhamnal is transformed into α-methylrhamnoside, which is identified as the acetate, m. p. 87°, $[\alpha]_D$ −53·5°. In like manner, an aqueous solution of cellobial, when treated with perbenzoic acid dissolved in ethyl acetate, readily yields 5-*glucosidomannose*,

$$OH\cdot\underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(CH_2\cdot OH)\cdot$$
$$O\cdot\underbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH,$$

lustrous crystals ($+H_2O$), m. p. (anhydrous) 175—176°, $[\alpha]_D$ +15·1° to +10·7°. It reduces Fehling's and ammoniacal silver solution. Its relationship to cellobiose is shown by its conversion into cellobiosazone, m. p. 198°; it does not give a sparingly soluble phenylhydrazone. It is hydrolysed by *N*-hydrochloric acid to mannose and glucose, and is slowly attacked by emulsin. It is converted by acetic anhydride and pyridine into the *octa-acetate*, needles, m. p. 196—197° (corr.), after softening at 194°, $[\alpha]_D^{17}$ +33·16° in *s*-tetrachloroethane.

Cellobial hexa-acetate contains a mobile acetyl group in the unsaturated portion of the molecule, which is removed by short treatment with boiling water, whilst at the same time a re-arrangement occurs in the dihydrofuran ring; re-introduction of the acetyl group gives a different hexa-acetate from which cellobial cannot be obtained. The *compound*, $C_{12}H_{15}O_9Ac_5$, crystallises in colourless needles, m. p. 121—124°, after softening at 120°, $[\alpha]_D^{22}$ +44·43° in *s*-tetrachloroethane, whilst the new *hexa-acetate* has m. p. 121—122° after softening at 118°. Hydrolysis with barium hydroxide solution gives a crystalline *compound*, m. p. 175—176°, which differs completely from cellobial and 5-glucosidomannose.

Triacetylglucal similarly yields a strongly reducing *compound*, $C_6H_{10}O_4$, m. p. 49—50°. H. W.

The Synthesis of Amylopectin by Phosphoric Esterification of the Erythroamyloses. SAMEC and (MLLE) ANKA MAYER (*Compt. rend.*, 1921, **173**, 321—322; cf. this vol., i, 397).—Using Neuberg's method of esterification (cf. *Biochem. Zeitsch.*, 1919, **100**, 3) the authors have obtained from the erythroamyloses a *calcium amylophosphate*, which by electrodialysis loses its calcium and gives a viscous jelly resembling amylopectin in its properties.

W. G.

Acetolysis of Polysaccharides. MAX BERGMANN and FRANZ BECK (*Ber.*, 1921, **54**, [*B*], 1574—1578).—The authors consider that in acetyl bromide they have found a hydrolytic agent which causes fission of the glucosidic linking in such a manner that the original point of attachment is indicated in the products by the entry of a characteristic substituent. The most important innovation consists in the application of the reagent in the presence of much hydrobromic acid (and generally of acetic acid). The complex mixture causes acetylation, hydrolysis, and bromination. In

accordance with the nature of the original saccharide, the entrance of the halogen atom may be restricted to the aldehyde group which functions in the glucoside formation, so that substances resembling acetylbromoglucose are formed, or the alcoholic group concerned in the formation of saccharide may be replaced by bromine, in which case the nature of the brominated sugar gives immediate evidence of the structure of the original glucoside or saccharide.

Rice starch is rapidly attacked by a saturated solution of hydrogen bromide in a mixture of acetyl bromide and glacial acetic acid, with the production of acetylbromoglucose in 85% yield. The same substance is obtained from maltose or its octa-acetate. Cellulose behaves differently, since, although rapidly dissolved, it is much more slowly hydrolysed, and, after several days, gives only 40% of the cellulose sugar in the form of penta-acetylglucose; brominated sugars are simultaneously formed, the nature of which has not yet been elucidated. Cellulose acetate, when treated similarly, gives considerable quantities of acetylbromocellobiose.

Triacetyl-γ-methylrhamnoside is converted in like manner into acetobromorhamnose, m. p. 71—72°, $[\alpha]_D^{22}$ −168·6° in *s*-tetrachloroethane; in this instance, the process is therefore accompanied by a structural change in the oxygen bridge and appears to be the direct reversal of the formation of γ-methylrhamnoside acetate from acetobromorhamnose. H. W.

Preparation of New Derivatives of the Carbohydrates $(C_6H_{10}O_5)_n$ and their Homologues. LEON LILIENFELD (Oe. Pat. 82866; from *Chem. Zentr.*, 1921, iv, 40—41).—Ethereal derivatives of the polyoses are prepared by treating these substances in alkaline solution or basic derivatives such as their alkaline earth, ammonium, zinc, silver, or lead compounds with alkylating agents such as halogen-substituted alcohols or alkyl sulphates. The reaction proceeds in two stages. In the first stage ethers soluble in water are obtained. By further alkylation, ethers are obtained which are insoluble in water. By the action of ethyl iodide or ethyl sulphate on starch in 10% sodium hydroxide solution, *starch ethyl ethers* are obtained which are distinguished by their solubility in water. The *ether* insoluble in hot water forms a white, pulverulent or flocculent mass soluble in cold water. Another *ether* is insoluble both in hot and cold water and forms a white powder. *Tragacanth ethyl ether*, similarly prepared, is a white or grey powder insoluble in hot or cold water. *Dextrin ethyl ether* has similar properties. *Inulin ethyl ether* forms a viscous mass insoluble in hot or cold water. The ethers are stable on heating and in the presence of acids and alkalis. Their solutions in organic solvents leave on evaporation transparent films which are chemically and physically resistant. G. W. R.

The Stability of Powders containing Cellulose Nitrates. R. FRIC (*Compt. rend.*, 1921, **173**, 82—84; cf. A., 1912, i, 73).—Using the method previously described (*loc. cit.*, and Duclaux,

this vol., i, 545), it is shown that cellulose nitrate powders undergo marked decomposition when submitted to the action of ultra-violet rays, the velocity of transformation being constant and approximately equal to that obtained when the powder is heated at 100°.

W. G.

Hexamethylenetetramine. I. FRIEDRICH L. HAHN and H. WALTER (*Ber.*, 1921, **54**, [*B*], 1531—1542).—A satisfactory constitutional formula for hexamethylenetetramine has not yet been proposed. This is probably due to the fact that an equilibrium, $4NH_4^{\cdot}+6CH_2O \rightleftharpoons [(N_4C_6H_{12})H]^{\cdot}+3H^{\cdot}+6H_2O$, is reached in acid solution so that it is difficult to decide whether a given fission product is present as such in the hexamethylenetetramine molecule. A promising line of attack appears to be in the examination of the quaternary hexamethylenetetramine salts, since in them the functions of one nitrogen atom are clearly defined and differentiated from those of the remaining nitrogen atoms. A large number of these compounds are now described. They are prepared by adding the second component, dissolved in chloroform if necessary, to a solution of hexamethylenetetramine in chloroform (1 gram in 10 c.c.). The precipitated salts are washed with chloroform and ether. They all dissolve readily in water and hot alcohol, and can frequently be recrystallised from the latter solvent. They are sparingly soluble or insoluble in the other media.

The following individuals are described: *methylhexamethylenetetrammonium methyl sulphate*, $C_6H_{12}N_4Me\cdot SO_4Me$, m. p. 158°, and *ammonium sulphate*, $C_6H_{12}N_4Me\cdot SO_4\cdot NH_4$ (from methylhexamethylenetetrammonium methyl sulphate and hexamethylenetetramine, from the methyl sulphate and ammonia or from formaldehyde, ammonia, and ammonium sulphate), m. p. 214—215°, *nitrate*, long, colourless needles, m. p. 201—202° (decomp.), *picrate* (from other salts and picric acid, from hexamethylenetetramine picrate and formaldehyde, and from trinitroanisole and hexamethylenetetramine), orange-yellow crystals, m. p. 204°, *chloride*, m. p. 186°, and *perchlorate*, m. p. 204°. *Bismethylhexamethylenetetrammonium sulphate*, m. p. 212°. *Ethylhexamethylenetetrammonium ethyl sulphate*, m. p. 114—115°, *nitrate*, m. p. 137°, *picrate*, sulphur-yellow crystals, m. p. 173—173·5°, and *perchlorate*, m. p. 141—142°. Additive compounds were not obtained with the methyl esters of boric, benzoic, salicylic, *o*-, *m*-, and *p*-chlorobenzoic, *m*-nitro- and trinitro-benzoic or formic acids. Hexamethylenetetramine gives additive *products* with the following acetic esters (the m. p. are placed within brackets after the name of the ester): methyl chloroacetate (143°); ethyl chloroacetate (198°); methyl bromoacetate (130°); ethyl bromoacetate (172°); methyl iodoacetate (142°); ethyl iodoacetate (169°). In these compounds the halogen atom is ionisable. Methyl dichloroacetate does not combine with hexamethylenetetramine, whereas methyl trichloroacetate gives a *compound*, plates, m. p. 142°. The following compounds have also been prepared: *Methylhexamethylenetetrammonium thiocyanate*, p-*toluenesulphonate*, m. p. 204—205°, and β-*naphthalenesulphonate*,

m. p. 213—214°. *Ethylhexamethylenetetrammonium benzenesulphonate*, m. p. 157°. n-*Propylhexamethylenetetrammonium benzenesulphonate*, m. p. 134°. iso*Propylhexamethylenetetrammonium benzenesulphonate*, m. p. 131°. *Benzylhexamethylenetetrammonium benzenesulphonate*, m. p. 169°, and *thiocyanate*, m. p. 172°, *allylhexamethylenetetrammonium benzenesulphonate*, m. p. 130°. The latter substance is converted by sodium carbonate solution into acraldehyde and by concentrated hydrochloric acid and alcohol into allylamine hydrochloride in satisfactory yield.

The preparation of n-*propyl benzenesulphonate*, a pale yellow liquid which readily decomposes when heated, of n-*propyl toluene*-p-*sulphonate*, a colourless liquid, b. p. 138°/cathode vacuum, and of *benzyl benzenesulphonate*, colourless crystals, which decompose when preserved, m. p. 59°, is described incidentally. H. W.

Aminoacylcholine Esters. I. Glycylcholine. HAROLD WARD DUDLEY (T., 1921, **119**, 1256—1260).

The Reaction of Taurine with α-Naphthylcarbimide. C. L. A. SCHMIDT (*Proc. Soc. Exp. Biol. Med.*, 1921, **18**, 204—205; from *Physiol. Abstr.*, 1921, **6**, 297).—Taurine reacts with α-naphthylcarbimide to form the corresponding hydantoic acid; this was identified by analysis of its barium salt. C. R. H.

Compound of Carbamide with Calcium Nitrate. C. BOSCH (U.S. Pat., 1369383; cf. A., 1918, i, 528; 1920, i, 150).—A compound corresponding with the formula $Ca(NO_3)_2,4CO(NH_2)_2$ is obtained by mixing the constituents in the required proportions in the presence of a small quantity of water and then drying, or by adding to a hot concentrated solution of calcium nitrate or to a melt of a hydrate of this salt a suitable proportion of carbamide and allowing crystallisation to ensue. Long exposure of the salt or its solutions to a high temperature should be avoided, as even temperatures below the boiling point may cause decomposition with precipitation of calcium carbonate. The double compound is easily soluble in water and does not liquefy if exposed to the air.

CHEMICAL ABSTRACTS.

Syntheses of Cyanic Acid and of Carbamide by Oxidation of Organic Substances: Amides, Nitriles, and Methylcarbylamine. R. FOSSE and G. LAUDE (*Compt. rend.*, 1921, **173**, 318—321; cf. A., 1919, i, 152, 313, 459; 1920, ii, 714, 779).—The amides of the monobasic acids on oxidation in ammoniacal solution give cyanic acid which can be converted into carbamide. Similarly, the various diamides and nitriles give varying yields of cyanic acid and carbamide, and methylcarbylamine yields the same products. W. G.

Action of Mercury Fulminate on Various Metals and Alloys. A. LANGHANS (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1921, **16**, 105—107).—A brief description is given of the properties and preparation of some metallic fulminates other than those of mercury

and silver. The action of mercury fulminate on various metals and alloys has been investigated by exposing them to its action when suspended in water, and in the dry state in a damp atmosphere. Aluminium is the most rapidly attacked; even after a few hours, extensive formation of alumina occurs. Magnesium is almost equally affected. There is appreciable action on copper and zinc, but none on nickel. The order in which the metals and alloys stand as regards resistance to the action of the fulminate is as follows, those most resistant being placed first: nickel, silver, tin, bismuth, fusible alloy, cadmium, iron, white metal, lead, copper, zinc, brass, magnesium, and aluminium. There is no apparent difference in the effects produced by the white and grey varieties of mercury fulminate. W. J. W.

Action of Normal Sodium Arsenite on Thiocyano-compounds. A. GUTMANN (*Ber.*, 1921, **54**, [*B*], 1410—1414).—Ethyl thiocyanate reacts with a boiling alkaline solution of sodium arsenite to form ethyl mercaptan, sodium cyanide, and normal sodium arsenate; with alcoholic potassium sulphide solution, it gives ethyl mercaptan and potassium thiocyanate. Allylthiocarbimide and sodium arsenite, on the other hand, give mainly sodium thioarsenite, ammonia, and a brownish-black, flocculent precipitate. Cyanamide and dicyanodiamide do not oxidise sodium arsenite. Cyanogen sulphide reacts readily in accordance with the equation: $NC{\cdot}S{\cdot}CN + Na_2O + Na_3AsO_3 = NaCN + NaCNS + Na_3AsO_4$, whilst with ethyl cyanoiminocarbonate reaction takes place smoothly: $NH{:}C(OEt){\cdot}CN + Na_3AsO_3 + H_2O = 2HCN + Na_3AsO_4 + EtOH$, thus indicating that the initial material has probably the constitution $OEt{\cdot}N{:}CH{\cdot}N{:}C$. H. W.

Conversion of Malonic Acid into Glycine and of Methylmalonic Acid into α-Alanine. THEODOR CURTIUS and WILHELM SIEBER (*Ber.*, 1921, **54**, [*B*], 1430—1437).—The course of the change is indicated by the scheme: $CO_2K{\cdot}CH_2{\cdot}CO_2Et + N_2H_4 \longrightarrow CO_2K{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 \longrightarrow CO_2H{\cdot}CH_2{\cdot}CO{\cdot}N_3 \xrightarrow{-N_2} [CO_2H{\cdot}CH_2{\cdot}N{:}C{:}O] \xrightarrow{+H_2O} CO_2H{\cdot}CH_2{\cdot}NH_2 + CO_2$.

Potassium hydrazinomalonate, m. p. 174°, is prepared in almost quantitative yield by heating potassium ethyl malonate with hydrazine hydrate on a boiling water-bath [*benzylidenehydrazinomalonic acid*, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh$, crystallises in thin needles, m. p. 162° (decomp.)]. The similarly-prepared *potassium hydrazinomethylmalonate* is a colourless crystalline powder, m. p. 120—122° (corresponding *benzylidene* compound, thin needles, m. p. 148°). When an aqueous solution of potassium hydrazinomalonate and sodium nitrite is covered with ether and treated with the calculated amount of dilute hydrochloric acid, *azidomalonic acid* is obtained, which, however, could not be isolated in the pure state owing to its gradual hydrolysis to malonic and hydrazoic acids, and could not be converted into a homogeneous urethane compound by means of alcohol. When the moist ethereal solution of the azido-acid is allowed to evaporate spontaneously,

it gives a crystalline *residue* which does not melt below 260° and which in all probability has the constitution $CO_2H\cdot CH_2\cdot NH\cdot CO_2H$ or $CH_2<\begin{matrix}CO-O\\ NH\cdot CO\end{matrix}$, since it gives glycine and carbon dioxide when treated with cold water. The conversion of the azido-acid into glycine is most advantageously effected by preservation of the diazotised solution of the hydrazino-acid for some time, followed by evaporation to dryness and treatment of the residue with alcoholic hydrogen chloride and isolation of the glycine ester hydrochloride.

Potassium hydrazinomethylmalonate in a similar manner yields *azidomethylmalonic acid*, a colourless, strongly acid liquid which decomposes only slowly when preserved; its conversion into methyl α-aminopropionate hydrochloride, m. p. 155—157°, is described. H. W.

Constitution of Grignard's Magnesium Compounds. JAKOB MEISENHEIMER and JOHANNES CASPER (*Ber.*, 1921, **54**, [*B*], 1655—1665).—The formulæ, $\begin{matrix}Et\\Et\end{matrix}>O<\begin{matrix}MgAlk\\Hal\end{matrix}$, $\begin{matrix}Et\\Et\end{matrix}>O<\begin{matrix}Alk\\MgHal\end{matrix}$, and $\begin{matrix}Et\\Et\end{matrix}>O<\begin{matrix}MgAlk\\Hal:OEt_2\end{matrix}$, which have been assigned to Grignard's compounds must be regarded as unsatisfactory, since they fail to account for the reactivity of the substances. The authors, therefore, propose to regard them as complex compounds of magnesium in which the central atom has the co-ordination number 4, thus: $\begin{matrix}Et_2O\\Et_2O\end{matrix}>Mg<\begin{matrix}Alk\\Hal\end{matrix}$. In this formula the alkyl group and halogen atom are united to the magnesium by main valencies, the ether molecules by subsidiary valencies. When brought into contact with acetone, etc., the latter, by virtue of its greater reaction energy, displaces a molecule of ether yielding the substance $\begin{matrix}Me_2CO\\Et_2O\end{matrix}>Mg<\begin{matrix}Alk\\Hal\end{matrix}$. Re-arrangement of the bonds within the complex then occurs by which the subsidiary bond between the magnesium and the carbonyl oxygen becomes a chief bond; the alkyl group which has thus become detached from the magnesium atom attaches itself to the chief bond of the carbonyl carbon atom which has simultaneously become free, and the vacant co-ordination position of the magnesium atom is taken by a molecule of ether, thus: $\begin{matrix}Me_2CAlk\cdot O\\Et_2O\end{matrix}>Mg<\begin{matrix}OEt_2\\Hal\end{matrix}$. This conception is in complete harmony with the observation of Ahrens and Stapler (A., 1905, i, 868) that magnesium bromide and iodide form dietherates from which one molecule of ether can be displaced readily by a molecule of aldehyde, ketone, or amine. It also explains the peculiar behaviour of allyl haloids towards magnesium; as the final product of these reactions a crystalline mass is obtained which consists entirely of the magnesium haloid dietherate, the allyl radicle being quantitatively contained in the ethereal solution in the form of diallyl. [The rate of loss of ether

from the magnesium haloid dietherates in a vacuum or when heated is fully described.] The course of the reaction is explained as follows: The primary reaction consists in the formation of a normal Grignard compound, $\frac{Et_2O}{Et_2O}{>}Mg{<}\frac{C_3H_5}{Br}$, from which a molecule of ether is immediately displaced by a further molecule of allyl bromide, $\frac{Et_2O}{C_3H_5Br}{>}Mg{<}\frac{C_3H_5}{Br}$. In this complex, the allyl residue of the alkyl haloid is only loosely attached by reason of the union of the bromine atom to the magnesium, which may be thus expressed: $C_3H_5\left[\frac{Et_2O}{Br}{>}Mg{<}\frac{C_3H_5}{Br}\right]$. As a consequence, when two such molecules come within range of one another, the allyl residue is readily detached, yielding diallyl. Simultaneously, a change in bonds occurs by which the second bromine atom becomes attached by a main valency to the magnesium atom and the diallyl group by a subsidiary valency. A hydrocarbon such as diallyl has, however, but little free valency, and is therefore readily displaced by the ether, thus giving a magnesium haloid dietherate. The peculiar ability of allyl haloids is due to the reactivity of the halogen atom in these compounds and the relatively large amount of the available valency of the halogen atom. It is to be expected further that allyl bromide would have the same power of displacing ether from any similarly constituted Grignard compound. This is shown to be the case, since allyl bromide is found to react with ethereal solutions of magnesium methyl, ethyl, or phenyl bromide to give the magnesium haloid dietherate, and butene, pentene, and allylbenzene respectively.

The catalytic activity of ether and tertiary amines in promoting the action between magnesium and alkyl haloids cannot be explained satisfactorily by the assumption of the formation of oxonium salts of the type $\frac{Et}{Et}{>}O{<}\frac{Me}{I}$, since in this case a mixture of magnesium methyl and ethyl iodides must result. This difficulty is overcome by considering that the action between ether or base and alkyl haloid proceeds only to the subsidiary valency stage,

$$\frac{Et}{Et}{>}O\cdots\cdots MeI,\ Alk_3N\cdots\cdots PhI,$$

which accounts thus for the unusual mobility of the halogen atom.

H. W.

Accelerated Formation of Magnesium Alkyl and Aryl Haloids. HARRY HEPWORTH (T., 1921, **119**, 1249—1256).

Mercury Di-*n*-butyl and some of its Derivatives. JULES TIFFENEAU (*Bull. Sci. Pharmacol.*, 1921, **28**, 65—69; from *Chem. Zentr.*, 1921, iii, 26).—Mercury di-*n*-butyl and its derivatives prepared by ordinary methods agree with the already known organic mercury compounds. *Mercury di*-n-*butyl*, $Hg(C_4H_9)_2$, is formed from *n*-butyl iodide and sodium amalgam in ethyl acetate solution, together with mercury butyl iodide; it is a colourless,

highly refracting liquid with a characteristic odour, b. p. 223—224°/760 mm.; b. p. 117—118°/10 mm.; *d* 1·817. *Mercury* n-*butyl hydroxide*, $C_4H_9 \cdot Hg \cdot OH$, forms spangles, m. p. 47°. *Mercury* n-*butyl hydrosulphide*, $C_4H_9 \cdot Hg \cdot SH$, prepared from the preceding compound by the action of hydrogen sulphide, is crystalline, m. p. 59°. *Mercury* n-*butyl chloride*, $C_4H_9 \cdot HgCl$, forms slender, lustrous needles, m. p. 125·5°; it gives a precipitate of silver chloride with alcoholic silver nitrate. *Mercury* n-*butyl fluoride*, $C_4H_9 \cdot HgF$, prepared from the hydroxide and hydrofluoric acid, forms crystals, m. p. 147°; the alcoholic solution decomposes on warming. *Mercury* n-*butyl bromide*, $C_4H_9 \cdot HgBr$, forms white, lustrous spangles, m. p. 128°. *Mercury* n-*butyl iodide*, $C_4H_9 \cdot HgI$, forms colourless spangles, m. p. 114°, turning yellow on exposure to light. *Mercury* n-*butyl cyanide* forms nacreous spangles, m. p. 40°. *Mercury* n-*butyl acetate*, $C_4H_9 \cdot Hg \cdot OAc$, forms slender, hygroscopic needles, m. p. 50—51°. G. W. R.

Synthesis of Alkylarylmethanes from Ketones and Phenols. ARNO MÜLLER (*Chem. Zeit.*, 1921, **45**, 632).—Hydrochloric acid with the addition of a small quantity of ferric chloride is the best catalyst for use in this synthesis; sulphuric acid, phosphoric acid, acetic acid, zinc chloride, and thorium oxide are useless. Of the ketones, acetone and monochloroacetone give the best results. W. P. S.

Preparation of True Acetylenic Hydrocarbons from βγ-Dibromopropylene. R. LESPIEAU (*Bull. Soc. chim.*, 1921, [iv], **29**, 528—535).—The method previously described (this vol., i, 490) has been extended to the preparation of certain other acetylenic hydrocarbons. Magnesium phenyl bromide reacts with βγ-dibromopropylene to give *β-bromo-γ-phenyl-Δ^α-propene*, $CH_2 \colon CBr \cdot CH_2Ph$, b. p. 102°/17 mm.; m. p. −12·5°; d^0 1·39, which with bromine yields *ββγ-tribromo-α-phenylpropane*, $CH_2Br \cdot CBr_2 \cdot CH_2Ph$, b. p. 175—176°/18 mm. This compound reacts with sodium ethoxide to give *αβ-dibromophenylpropene*, which when reduced with zinc dust and alcohol gives *γ-phenyl-Δ^α-propinene*, b. p. 70—71°/20 mm., giving a crystalline *silver* salt and a *copper* salt. Similarly, starting with magnesium *cyclo*hexyl bromide, the compounds obtained are *β-bromo-γ-*cyclo*hexyl-Δ^α-propene*, $CH_2 \colon CBr \cdot CH_2 \cdot C_6H_{11}$, b. p. 82°/10 mm.; d^{16} 1·24; n_D^{16} 1·501; *ββγ-tribromo-α-*cyclo*hexylpropane*, not isolated in the pure state; and *γ-*cyclo*hexyl-Δ^α-propinene*, b. p. 157—160°, giving a *silver* salt. These acetylenic hydrocarbons may also be obtained by the action of the magnesium alkyl or aryl bromide on αβγ-tribromopropylene. W. G.

Experiments with ω-Trifluorotoluene. FRÉD SWARTS (*Bull. Acad. roy. Belg.*, 1920, 389—398; from *Chem. Zentr.*, 1921, iii, 32; cf. A., 1899, i, 197).—By heating ω-trifluorotoluene with four times the quantity of hydrobromic acid (*d* 1·79) in the presence of amorphous silica, benzoic acid is obtained quantitatively by the following stages, $CPhF_3 + HBr = CPhBrF_2 + HF$; $CPhBrF_2 + 2H_2O = Ph \cdot CO \cdot OH + HBr + 2HF$. In the presence of

iron or copper, the side group is not attacked even at 350°. By nitration at 0°, *ω-trifluoro-*m*-nitrotoluene* is obtained, b. p. 102—103°/40 mm., together with traces of the other isomerides. These may be isolated by transformation into the trifluorotoluidides, the acetyl compounds of which are easily separated by fractional crystallisation. m-*Acetotrifluorotoluidide* has m. p. 103·5°. The results obtained with the nitration of ω-trifluorotoluene are in disagreement with the contention of Hollemann ("Substituierung im Benzolkern," p. 479) that the orientation of a radicle is not altered when one of the elements in it is replaced by a substituent of similar behaviour to the radicle. G. W. R.

Catalytic Hydrogenation of Organic Fluorine Derivatives. FRÉD SWARTS (*Bull. Acad. roy. Belg.*, 1920, 399—417; from *Chem. Zentr.*, 1921, iii, 32—33).—The catalytic hydrogenation of organic fluorine derivatives by molecular hydrogen and platinum black proceeds differently according as the fluorine is substituted in an aromatic nucleus or in a side chain. Fluorine derivatives of the *cyclo*hexane series may be prepared without attacking the side chain. The reduction of *p*-fluorobenzoic acid in the aqueous solution of its sodium salt proceeds in two well-defined stages, benzoic acid being formed at first and *cyclo*hexanecarboxylic acid more slowly afterwards. In the hydrogenation of fluorobenzene, the two stages are not so well defined. Silicon tetrafluoride and hydrofluoric acid have no effect on the activity of the catalyst.

The hydrogenation of ω-trifluorotoluene, $CPhF_3$ (see preceding abstract), gives exclusively *trifluoromethyl*cyclo*hexane*, a colourless liquid of unpleasant odour; d^{15} 1·0870; $d^{11·5}$ 1·09800; b. p. 107·05°/761·5 mm.; liquid at −78°; n_α 1·37661 (at 11·5°), n_D 1·37945, n_β 1·38379, n_γ 1·38704. ω-Difluorotoluene gives by hydrogenation *difluoromethyl*cyclo*hexane*, a colourless liquid similar to the preceding compound, which has b. p. 125·25°/759 mm.; $d^{17·5}$ 1·01675. A little methyl*cyclo*hexane is also formed. The $-CHF_2$ group is thus slowly reduced and shows less stability than the $-CF_3$ group, a result that was expected from thermochemical considerations. ω-*Difluorochlorotoluene* gives on hydrogenation difluorotoluene, toluene, and methyl*cyclo*hexane. It is not known whether toluene and methyl*cyclo*hexane are formed from difluorotoluene in the reaction. The presence of chlorine in the side group renders the fluorine less stable, and toluene may be formed by direct reduction. More silicon tetrafluoride is formed in the reduction of difluorochlorotoluene than in the case of difluorotoluene. The hydrogenation of difluoroethyl alcohol gave no positive result. G. W. R.

The Action of the Grignard Reagent on certain Tervalent Organo-iodo-compounds. HARRY HEPWORTH (T., 1921, **119**, 1244—1249).

Additive Compounds of *m*-Dinitrobenzene. D. D. KARVÉ and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1921, **4**, 159—176).—The ability of *m*-dinitrobenzene to form additive compounds with

a number of classes of organic substances has been investigated. In many cases the additive compound has been isolated by crystallising a mixture of the two components from alcohol. Where no definite compound could be isolated under such conditions, the freezing-point curve (temperature–concentration curve) has in many cases been examined.

The combining capacity of *m*-dinitrobenzene is much less pronounced than that of *s*-trinitrobenzene or of α- and β-tetranitronaphthalenes. Many addenda which combine with these latter do not form definite compounds with *m*-dinitrobenzene. Among the compounds that have been prepared, the molecular ratio between the nitro-compound and the addendum is the same with *m*-dinitrobenzene as with *s*-trinitrobenzene. The colours of the dinitro-compounds are a shade lighter and the melting points considerably lower than those of the corresponding trinitro-compounds.

Individual *compounds* are described of *m*-dinitrobenzene with the following addenda: acenaphthene, $C_{12}N_{10},C_6H_4(NO_2)_2$, lemon-yellow needles, m. p. 73·5°; β-naphthylamine, dark red needles, m. p. 57°; benzeneazo-β-naphthylamine, deep red, lustrous prisms, m. p. 66°; aminobenzeneazodimethylaniline, short, brown needles, m. p. 115°; 1 : 5-naphthalenediamine, brownish-black crystals, m. p. 78—79°; 3 : 3′-diaminoazobenzene, lustrous, brown needles, m. p. 90—91°; 4-aminoazonaphthalene, $C_{10}H_7N_2{\cdot}C_{10}H_6{\cdot}NH_2,2C_6H_4(NO_2)_2$, dark red, microscopic needles, m. p. 122°; benzyl-α-naphthylamine, dark orange needles, m. p. 63·5°; 4 : 4′-diaminodiphenylamine, violet-black needles, m. p. 91—92°; 3 : 3′-diaminostilbene, feathery, orange needles, m. p. 108—109°; 3-aminocarbazole, violet-brown prisms, m. p. 83—84°; *o*-aminoquinoline, orange leaflets, m. p. 103—104°; *p*-aminoquinoline, red prisms, m. p. 89—90°; *p*-aminotetrahydroquinoline, pale brown needles, m. p. 91—92°; 2-amino-6-methylquinoline, orange-red plates, m. p. 74—74·5°.

According to investigations of the freezing-point curves, *m*-dinitrobenzene does not yield additive compounds with the following substances: fluorene, anthracene, phenanthrene, diphenyl, triphenylmethane, retene, 2 : 4-dichloroaniline, 2 : 6-dibromoaniline, 2 : 4 : 6-tribromoaniline, *o*-, *p*-, and *m*-nitroaniline, 4-acetylamino-1-phenylazonaphthalene, *p*-aminobenzophenone, *p*-leucaniline, diphenylamine, *p*-aminodiphenylamine, thiodiphenylamine, phenyl-β-naphthylamine, acetanilide, dimethylaniline, dimethyl-α-naphthylamine, tetramethyldiaminothiobenzophenone, dibenzylaniline, carbazole, αα-diphenylpyridine, β-imino-α-cyanohydrindene, 3-phenylpyrazolone, 1-phenyl-3-methylpyrazolone, phenylacridine, quinoline, *iso*quinoline, tetrahydroquinoline, tetrahydro*iso*quinoline, 6- and 8-methylquinoline and the corresponding tetrahydro-compounds, α- and β-naphthaquinoline, carbostyril, 2 : 3 : 5-triphenylpyrrole, β-naphthol, β-naphthyl ethyl ether, dimethylaniline disulphide, acetophenoneoxime, benzaldehydephenylhydrazone.

β-Tetranitronaphthalene forms additive *compounds* with the following substances: *p*-aminoazonaphthalene,

$$2C_{10}H_4(NO_2)_4,NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_7,$$

chocolate powder, m. p. 240°, aminobenzeneazodimethylaniline,

$2C_{10}H_4(NO_2)_4,NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2$, black leaflets, m. p. 206—207°; tetramethyldiaminobenzophenone,

$$2C_{10}H_4(NO_2)_4,CO(C_6H_4{\cdot}NMe_2)_2,$$

black plates, m. p. 207—208°. It does not unite with tetramethyldiaminodiphenylmethane. H. W.

The Sulphonation of Toluene with Chlorosulphonic Acid. LEONARD HARDING (T., 1921, **119**, 1261—1266).

Preparation of *ar*-Tetrahydronaphthalenesulphonic Acids, their Chlorides and Derivatives. TETRALIN G. M. B. H., Berlin (D.R.-P. 336615; from *Chem. Zentr.*, 1921, iv, 125—126).—Tetrahydronaphthalene is treated at low temperatures with chlorosulphonic acid and the resultant mixture separated after hydrolysis or transformation into suitable derivatives. For example, chlorosulphonic acid cooled to −5° is added to tetrahydronaphthalene with agitation, the temperature being maintained below 5°. After separation of the theoretical amount of hydrochloric acid the products are poured into cold water and the light yellow powder, consisting of about equal parts of 1- and 2-tetrahydronaphthalenesulphonyl chloride, separated by filtration. The acids are obtained by treatment with steam. After evaporation to dryness in a vacuum, *tetrahydronaphthalene-1-sulphonic acid* is obtained by extraction of the residue with chloroform and crystallisation and forms monohydrated crystals, m. p. 105—110°. *Tetrahydronaphthalene-2-sulphonic acid* remains in the residue and may be recrystallised from dilute sulphuric acid. The mixed sulphonyl chlorides on treatment with ammonia solution give mixed amines with development of heat. These dissolve in sodium hydroxide solution on warming, and on cooling the *sodium* salt of tetrahydronaphthalene-2-sulphonamide, $C_{10}H_{11}{\cdot}SO_2{\cdot}NHNa$, is obtained, which by treatment with acids gives free *tetrahydronaphthalene-2-sulphonamide*, crystals, m. p. 137°. By the action of acids or carbon dioxide on the alkaline mother-liquor, the *tetrahydronaphthalene-1-sulphonamide* is obtained as crystals, m. p. 137—140°. (The isomerides, which have almost the same melting point, show a depression of melting point to 110—115° when mixed.) *Tetrahydronaphthalene-1-sulphonyl chloride*, obtained from the 1-sulphonamide by way of the acid, has m. p. 70—72°; it gives with aniline, *tetrahydronaphthalene-1-sulphonanilide*. By the action of zinc dust on a suspension of the sulphonyl chlorides in water a mixture of crystals of the zinc salts of the corresponding *sulphinic acids* is obtained. Complete reduction with fuming hydrochloric acid and zinc dust gives a mixture of α- and β-*tetrahydronaphthylthiols*, an oil, b. p. 143—147°/15 mm., which gives white needles with alcoholic mercuric chloride solution. Oxidation of the alcoholic ammoniacal solution by air gives the corresponding *disulphides*, $S_2(C_{10}H_{11})_2$. By treating a solution of the mixture of α- and β-tetrahydronaphthylthiols in 2*N*-sodium hydroxide solution with monochloroacetic acid, warming for a short time, and treating the cooled mixture with ammonium chloride solution, the *ammonium* salt of 2-*tetrahydronaphthylthiolacetic acid* separates

in crystalline leaflets. The free *acid*, obtained by treatment with hydrochloric acid, has m. p. 69—70°, and is identical with the product obtained from the 2-sulphonyl chloride by way of the sulphonic acid and thiol. 1-*Tetrahydronaphthylthiolacetic acid* is obtained from the mother-liquors after the crystallisation of the ammonium salt of the 2-acid by precipitation with hydrochloric acid; it forms crystals, m. p. 133—135°. Both thiolacetic acids, especially the 2-acid, are readily transformed into "tetrahydronaphthalenethioindigo." G. W. R.

Action of Sodammonium on Diphenylmethane, Fluorene, and Indene. Dimethylfluorene. P. LEBEAU and M. PICON (*Compt. rend.*, 1921, **173**, 84—86).—Diphenylmethane reacts only slowly and very incompletely with sodammonium, giving a sodium derivative. Fluorene reacts readily to give a substituted sodium derivative, although a portion of the fluorene at the same time undergoes hydrogenation. The sodium derivative of fluorene acts on methyl chloride to give *dimethylfluorene*, m. p. 95—96°; b. p. 286·5°/764 mm., yielding a *tetrahydro*-derivative, b. p. 280—281°/762 mm.; 148—149°/20 mm. Indene behaves in the same way with sodammonium, but a much larger proportion of the indene undergoes hydrogenation. W. G.

Tetranitromethane. IV. Conversion of Tertiary Amines into Secondary Nitrosoamines. ERICH SCHMIDT and RICHARD SCHUMACHER (*Ber.*, 1921, **54**, [*B*], 1414—1419; cf. A., 1920, i, 727).—Further examples of the conversion of fatty aromatic tertiary amines into secondary nitrosoamines by tetranitromethane in the presence of pyridine are given. The method is applied to aliphatic tertiary amines in the presence of acetic acid.

m-Bromodimethylaniline, m. p. 11°, b. p. 100—104°/2 mm., gives m-*bromophenylmethylnitrosoamine*, colourless crystals, m. p. 43—44°, in 89% yield. *p*-Bromophenylmethylnitrosoamine, colourless needles, m. p. 73—74°, is obtained from *p*-bromodimethylaniline, the yield being 93%, whilst 2 : 4-dichlorodimethylaniline, b. p. 92—95°/2 mm., gives a 92% yield of 2 : 4-*dichlorophenylmethylnitrosoamine*, yellowish-white needles, m. p. 53—54°. Tri-*n*-propylamine (1 mol.) dissolved in acetic acid (2 mols.) is transformed by an alcoholic solution of tetranitromethane (1·1 mols.) in a sealed tube at 100° into di-*n*-propylnitrosoamine, b. p. 59—61°/1·5 mm., the yield being 92·3% of that theoretically possible. Di*iso*butylnitrosoamine, b. p. 68°/1·3 mm., di*iso*amylnitrosoamine, b. p. 100—102°/2·5 mm., and diethylnitrosoamine, b. p. 61—63°/12 mm., are prepared similarly. *m*-Nitrodimethylaniline is converted by the same method into *m*-nitrophenylmethylnitrosoamine, m. p. 74—75°, in 95·4% yield. H. W.

Transformation and Hydrolysis of Toluene-*p*-sulphonyl-*p'*-anisidide and its *N*-Methyl Derivative. J. HALBERKANN (*Ber.*, 1921, **54**, [*B*], 1665—1675).—Treatment of the substances named with acid results in hydrolysis or in a wandering of the *p*-toluenesulphonyl group such as has been described by Witt and Truttwin (A., 1914, i, 228) and Witt and Uerményi (A., 1913, i, 360).

p-*Toluenesulphonyl*-p-*anisidide*, long, colourless, prismatic needles, m. p. 113—114°, is converted by methyl sulphate in aqueous alkaline solution into N-p-*toluenesulphonylmethyl*-p-*anisidide*, $OMe\cdot C_6H_4\cdot NMe\cdot SO_2\cdot C_6H_4Me$, prismatic rods, m. p. 68—69°. The latter substance is converted by a mixture of sulphuric acid (*d* 1·84) and glacial acetic acid into 2-*methylamino*-5-*methoxyphenyl*-p-*tolyl-sulphone*, $C_6H_4Me\cdot SO_2\cdot C_6H_3(OMe)\cdot NHMe$, large, colourless, acute prisms, m. p. 150°, which is characterised as a secondary base by the isolation of its *nitroso*-derivative, coarse, colourless rhombohedra, m. p. 86—87°, and *acetyl* compound, four-sided needles, m. p. 138°. The action of sulphuric acid in aqueous solution of varying concentration on *N*-*p*-toluenesulphonylmethyl-*p*-anisidide at 150° has been systematically examined; solutions containing up to 40% of acid have but little action owing to the sparing solubility of the original materials. Better results are obtained with 50% acid, but the highest yields (60%) of volatile base (*N*-methyl-*p*-anisidine, colourless leaflets, m. p. 35—36°) are obtained with 60% acid, whereby the remainder of the original substance is in part unchanged and in part transformed. A 70% acid causes complete transformation even at 120°.

Sulphuric acid (*d* 1·84) converts toluene-*p*-sulphonyl-*p*-anisidide mainly into *p*-aminophenol-3-sulphonic acid, cubes or plates, or ($+H_2O$), needles, the crystalline form depending on the temperature of crystallisation; in addition, small amounts of 2-*amino*-5-*methoxyphenyl*-p-*tolylsulphone*, $C_6H_4Me\cdot SO_2\cdot C_6H_3(NH_2)\cdot OMe$, are also produced. Better yields of the latter substance (35%) are obtained by the action of sulphuric acid (*d* 1·73) during an hour at 110°. It crystallises in almost colourless prisms, m. p. 148°, and yields an unstable *hydrochloride*, long, colourless needles, and an *acetyl* derivative, needles, m. p. 134°. As a primary amine, the substance can be diazotised, and thus yields the following compounds by coupling with phenols in alkaline solution and with *m*-phenylenediamine in acid solution: *bis*-[4'-*methoxy*-2'-p-*toluenesulphonylbenzeneazo*]-4 : 6-*dihydroxybenzene*,

$$[C_7N_7\cdot SO_2\cdot C_6H_3(OMe)\cdot N{:}N]_2C_6H_2(OH)_2,$$

slender, orange-red needles, m. p. 272° (decomp.), after darkening above 250°; 4'-*methoxy*-2'-p-*toluenesulphonylbenzeneazo*-2 : 4-*dihydroxybenzene*, $C_7H_7\cdot SO_2\cdot C_6H_3(OMe)\cdot N{:}N\cdot C_6H_3(OH)_2$, coarse, brownish-red needles, m. p. 219°; 4'-*methoxy*-2'-p-*toluenesulphonylbenzeneazo*-β-*naphthol*, $C_7H_7\cdot SO_2\cdot C_6H_3(OMe)\cdot N{:}N\cdot C_{10}H_6\cdot OH$, bright red needles, m. p. 203°; 4'-*methoxy*-2'-p-*toluenesulphonylbenzeneazo*-m-*phenylenediamine hydrochloride*, violet-red needles. 2-*Amino*-5-*hydroxyphenyl*-p-*tolylsulphone*, from the methyl ether and hydrochloric acid at 150°, forms colourless prisms, m. p. 150°. H. W.

The Formation and Properties of Dithioketones ($R_2C{:}S{:}S$) and Dithio-ethers ($R_2S{:}S$). II. KUVERJI GOSAI NAIK (T., 1921, **119**, 1231—1242).

Nitro- and Amino-derivatives of Methylethylbenzene. ALPHONSE MAILHE (*Compt. rend.*, 1921, **173**, 160—162).—1-Methyl-3-ethylbenzene when nitrated in the cold with fuming nitric acid

in acetic acid gives 6-*nitro*-1-*methyl*-3-*ethylbenzene*, b. p. 245°, which on reduction with nickel at 250° gives 6-*amino*-1-*methyl*-3-*ethylbenzene*, b. p. 228—229°, giving a *hydrochloride*, m. p. 152°. The amine reacts with various organic acids to give the following derivatives: *formyl*, m. p. 151°, *acetyl*, m. p. 105°; *propionyl*, b. p. 318—320°; *butyryl*, m. p. 72°; iso*valeryl*, m. p. 68°, and *benzoyl*, m. p. 152°. With phenylcarbimide it gives *di*-1-*methyl*-3-*ethylphenyl*-6-*carbamide*, m. p. 105°. It condenses with aldehydes to give Schiff's bases, namely, 6-*benzylideneamino*-1-*methyl*-3-*ethylbenzene*, b. p. 330°, and 6-iso*valerylideneamino*-1-*methyl*-3-*ethylbenzene*, b. p. 268—270°. With glycerol and sulphuric acid in the presence of nitrobenzene, 6-amino-1-methyl-3-ethylbenzene yields 8-*methyl*-6-*ethylquinoline*, b. p. 273—275°. By alkylation in the presence of aluminium oxide at 380—400° the amine gives 6-*dimethylamino*-1-*methyl*-3-*ethylbenzene*, b. p. 217°, and 6-*diethylamino*-1-*methyl*-3-*ethylbenzene*, b. p. 235°.

When nitrated without precaution with sulphuric and nitric acids, methylethylbenzene gives dinitrobenzene-1 : 3-dicarboxylic acid, m. p. 215°, but if the nitration is carried out slowly the product is s-*trinitro*-1-*methyl*-3-*ethylbenzene*, m. p. 90°. W. G.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXIX. The Binary Systems of *m*-Aminophenol with Amines. ROBERT KREMANN and HEINZ HOHL (*Monatsh.*, 1920, **41**, 613—630; cf. this vol., i, 561).—*m*-Aminophenol and *p*-toluidine form a compound (1 : 1), which is considerably dissociated in the fused mixture; the eutectic with *p*-toluidine lies at 37° and corresponds with 13% of *m*-aminophenol. The system: aniline–*m*-aminophenol gives two curves meeting in a eutectic at −16° with 85% of aniline. α-Naphthylamine and *m*-aminophenol yield a simple eutectic at 36° and 84% of the amine. β-Naphthylamine and *m*-aminophenol yield a compound (1 : 1), m. p. 91°, the eutectics corresponding with 90·5° and 51% of the amine, and with 90° and 71% of the amine.

With *o*- and *m*-phenylenediamines, *m*-aminophenol forms, not compounds, but only eutectics: (*o*-) 63° and 55% and (*m*-) 24° and 63% of the diamine. The system: *m*-aminophenol–*p*-phenylenediamine forms two compounds: 2 mols. *m*-aminophenol : 1 mol. *p*-phenylenediamine, m. p. 97°, and the 1 : 1-compound, m. p. 102·5°; the eutectics between *m*-aminophenol and the 2 : 1-compound between the 2 : 1- and the 1 : 1-compounds, and between the 1 : 1-compound and *p*-phenylenediamine, corresponding respectively with 94° and 23%, 95° and 38%, and 101° and 56% of the diamine.

The system: *p*-aminophenol–*p*-toluidine exhibits no signs of the formation of a compound, but gives a eutectic at 41° corresponding with 95% of *p*-toluidine. T. H. P.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXX. The Binary Systems of Diphenylmethane with Phenols and Amines. ROBERT KREMANN and JULIUS FRITSCH (*Monatsh.*, 1920, **41**, 631—653).—The binary

systems, diphenylmethane with α- and β-naphthylamines and *p*-phenylenediamine furnish no evidence for the existence of compounds in the solid state; the eutectics lie at 9·5°, 21·4°, and 23·3° respectively, and correspond with 63%, 95%, and about 99% respectively of diphenylmethane.

Similarly, diphenylmethane forms no compound with α-naphthol, β-naphthol, catechol, or quinol, the eutectics in the respective systems lying at 19·6°, 22·6°, 23·1°, and 23·9°, and corresponding with 92·5%, 95·0%, 99·0%, and almost 100% of diphenylmethane. Further, diphenylmethane forms no compound with resorcinol or pyrogallol, but the binary systems show solubility gaps.

With *m*- or *p*-nitrophenol or picric acid, diphenylmethane forms no compounds; the eutectics in the three binary systems lie at 22°, 23°, and 22·5° respectively, and correspond with 97, 99—100, and 93 mol.% of diphenylmethane. T. H. P.

Tautomerism of Resorcinol. J. Herzig and S. Zeisel (*Ber.*, 1921, **54**, [*B*], 1403—1407).—A question of priority (cf. Herzig and Zeisel, A., 1920, i, 732; Fuchs, A., 1920, i, 545; this vol., i, 241). H. W.

The 1 : 2-*cyclo*Heptanediols and the Suppleness of the Saturated Rings. J. Böeseken and H. G. Derx (*Rec. trav. chim.*, 1921, **40**, 529—531).—A preliminary paper giving an account of the preparation of the two isomeric 1 : 2-*cyclo*heptanediols from *cyclo*heptene. The *cis*-isomeride, m. p. 46°, is obtained by oxidising *cyclo*heptene with potassium permanganate and magnesium sulphate. It gives a *dioxymethylene* derivative, b. p. 199°. For the preparation of the *trans*-isomeride, m. p. 63°, the *cyclo*heptene is oxidised with peroxybenzoic acid in chloroform solution and the product hydrated by treatment with dilute hydrochloric acid. It gives a *dioxymethylene* derivative, b. p. 197°. The method of distinguishing between *cis*- and *trans*-isomerides by the action of acetone is not therefore applicable to seven-carbon ring compounds. W. G.

The Distinction and Separation of Cyclic *cis*- and *trans*-1 : 2-Diols by means of Acetone. J. Böeseken and H. G. Derx (*Rec. trav. chim.*, 1921, **40**, 519—524).—The *cis*-isomerides of the cyclic 1 : 2-diols condense with acetone in the presence of a little hydrogen chloride to give compounds containing a dioxymethylene ring, whereas under the same conditions the *trans*-isomerides do not react. The *cis*-condensation compound can readily be isolated and then reconverted into the diol by boiling with dilute acids.

In this way it is shown that of the tetrahydronaphthalene-2 : 3-diols the *cis*-isomeride has m. p. 120°, and gives with acetone a *condensation* product, m. p. 78—79°, whilst the *trans*-isomeride has m. p. 135°. Of the tetrahydronaphthalene-1 : 2-diols, the *cis*-isomeride has m. p. 102°, and gives with acetone a *condensation* product, b. p. 105°/2 mm.; $n_D^{18·5}$ 1·52613; $d_4^{18·5}$ 1·0812, whilst the *trans*-isomeride has m. p. 112—113°. W. G.

Action of Organomagnesium Compounds on Arylsulphonic Chlorides. E. WEDEKIND and D. SCHENK (*Ber.*, 1921, **54**, [*B*], 1604—1612).—Chlorides and esters of sulphonic acids, at any rate in the aromatic series, behave qualitatively and quantitatively differently from chlorides and esters of carboxylic acids towards organomagnesium derivatives. Assuming the formation of an intermediate product of the type $R\cdot SR'_3(OH)_2$, the chief types of action may be represented by the schemes: (1) $Ar\cdot SEt_3(OH)_2 \longrightarrow Ar\cdot S\cdot Et+2EtOH$, (2) $2Ar\cdot SMe_3(OH)_2 \longrightarrow Ar\cdot S_2O_2\cdot Ar+2H_2O+3C_2H_6$, (3) $Ar\cdot SPh_3(OH)_2 \longrightarrow Ar\cdot SO\cdot Ph+Ph\cdot Ph+H_2O$, and (4) $C_7H_7\cdot SO_2Cl+MgPhBr \longrightarrow C_7H_7\cdot SO_2Ph$. In general, reaction leads to the production of a number of compounds and its exact course is influenced by the specific nature of the components.

p-Toluenesulphonyl chloride is converted by an ethereal solution of magnesium ethyl bromide into ethyl *p*-tolyl sulphide, b. p. 117—119°/34 mm., di-*p*-tolyl disulphoxide, m. p. 87—88°, and magnesium *p*-toluenesulphonate. *p*-Toluenesulphonyl chloride and magnesium methyl iodide yield p-*tolyl methyl sulphide*, a colourless liquid, b. p. about 104—105°/20 mm., and di-*p*-tolyl disulphoxide, the latter being in this case (in contrast with the former instance) the main product of the change. Benzenesulphonyl chloride and magnesium phenyl bromide give diphenyl, diphenyl sulphide, and (as main product) diphenyl sulphoxide. Diphenyl, phenyl-*p*-tolylsulphone, phenyl-*p*-tolyl sulphoxide (?), and magnesium toluene-*p*-sulphonate are obtained from *p*-toluenesulphonyl chloride and magnesium phenyl bromide. The action of magnesium α-naphthyl and camphor bromides on *p*-toluenesulphonyl chloride does not yield homogeneous products.

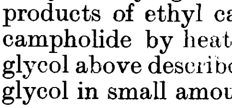
Magnesium ethyl bromide reacts slowly with ethyl toluene-*p*-sulphonate in ethereal solution, giving, as main product, magnesium toluene-*p*-sulphonate (cf. Ferns and Lapworth, T., 1912, **101**, 297). H. W.

Thiophenols. IV. Thiophenol Ethers of Triphenylmethane and the Auxochromic Action of Alkylthiol Groups. K. BRAND and OTTO STALLMANN (*Ber.*, 1921, **54**, [*B*], 1578—1585).—The introduction of the methylthiol group into triphenylcarbinol has been effected in several positions. As is to be expected, this group is more pronouncedly auxochromic in its action than is the methoxyl radicle, and the effect when in the *ortho*-position to the central carbon atom is greater than when in the *para*-position.

o-Nitrophenyl methyl sulphide, m. p. 64—65°, is conveniently prepared by the reduction of the corresponding disulphide by sodium hydroxide and sodium sulphide. It is slowly converted by methyl sulphate into o-*nitrophenyldimethylsulphonium methosulphate*, $NO_2\cdot C_6H_4\cdot SMe_2\cdot O\cdot SO_2\cdot OMe$, colourless crystals, m. p. 155—157° (decomp.), which is transformed by potassium iodide into the corresponding *iodide*, unstable, yellow needles, m. p. 79—81° (decomp.). *o*-Aminophenyl methyl sulphide, prepared by the reduction of the nitro-compound with zinc filings and hydrochloric acid, b. p. 234°/atmospheric pressure, 133—134°/15 mm., is con-

verted by Sandmeyer's reaction into *o-bromophenyl methyl sulphide*, a colourless, highly refractive liquid, b. p. 256°/768 mm., and small quantities of diphenylene disulphide, m. p. 158°. The bromo-compound reacts normally with magnesium in the presence of ether, and the product gives *o-methylthioltriphenylcarbinol*, $OH\cdot CPh_2\cdot C_6H_4\cdot SMe$, broad, colourless needles, m. p. 95·5—96°, with benzophenone and *oo'-dimethylthioltriphenylcarbinol*, colourless leaflets, m. p. 136°, with ethyl benzoate. H. W.

Preparation of Glycols Corresponding with Pinic, Norpinic, and *d*-Camphoric Acids and their Derivatives. G. J. Östling (*Öfvers. Finska Vet.-Soc.*, 1914, **57**, [*A*], No. 7, 19 pp.; from *Chem. Zentr.*, 1921, iii, 105—106).—2 : 2-*Dimethyl*-1 : 3-*dimethanol*cyclo*butane*, $OH\cdot CH_2\cdot CH<\substack{CH_2\\ CMe_2}>CH\cdot CH_2\cdot OH$, is prepared by acting on an alcoholic solution of diethyl norpinate with metallic sodium at 140°, adding water, and heating for some hours, distilling off the alcohol, and extracting the alkaline solution with ether. It is a viscous liquid of aromatic odour, b. p. 150—152°/15 mm. The *dibromide*, $C_8H_{14}Br_2$, is a colourless liquid with b. p. 128—130°/10 mm. 2 : 2-*Dimethyl*-1-*methanol*-3-β-*ethanol*cyclo*butane*, $OH\cdot CH_2\cdot CH<\substack{CH_2\\ CMe_2}>CH\cdot CH_2\cdot CH_2\cdot OH$, the glycol corresponding with pinic acid, prepared similarly, is a liquid, b. p. 166—167°/117 mm. The *dibromide*, $C_9H_{16}Br_2$, is a liquid, b. p. 144—145°/10 mm. *Methyl camphorate*, prepared by the action of an alcoholic solution of camphoric acid on methyl sulphate in the presence of potassium hydroxide at the ordinary temperature, has b. p. 133°/13 mm., $d_4^{14\cdot6}$ 1·0799, n_D^{19}, 1·46271, $[\alpha]_D+49\cdot07°$. This and the diethyl salt, as in the case of norpinic acid esters, give, on reduction, 1 : 2 : 2-*trimethyl*-1 : 3-*dimethanol*cyclo*pentane* (annexed formula), forming long needles, m. p. 126—127°. The corresponding *oxide*, $C_{10}H_{18}O$, is prepared by heating the glycol with hydrochloric acid; it forms leaf-like crystals of camphor-like odour, m. p. 176°.



By acidifying the residue obtained after removing the reduction products of ethyl camphorate, an oily acid is obtained which gives campholide by heating in a vacuum. This by reduction gives the glycol above described. Reduction of camphoric anhydride gives the glycol in small amounts as well as campholide and camphoric acid. G. W. R.

Formation of Bicyclic Systems with *cyclo*Butane Rings. G. J. Östling (*Öfvers. Finska Vet.-Soc.*, 1915, **57**, [*A*], No. 23, 14 pp.; from *Chem Zentr.*, 1921, iii, 106).—An attempt to prepare a bicyclic *cyclo*butane compound by acting on the dibromide obtained from the glycol of pinic acid (see preceding abstract) with sodium was unsuccessful. By the action of sodium on ethyl pinate complex products were obtained. The dry distillation of lead pinate gave a *ketone*, $C_8H_{12}O$, of pleasant odour, b. p. 93—95°/25 mm.; $d_4^{19\cdot5}$ 0·9448; n_D^{18} 1·4755; it is probably identical with the substance obtained

by the distillation of calcium pinate (Bousdorff, A., 1912, i, 34). The *semicarbazone* has m. p. 160°. Dry distillation of calcium camphorate gave a good yield of camphoric anhydride. G. W. R.

1 : 2 : 2-Trimethyl-1 : 3-dimethanol*cyclo*pentane. G. J. ÖSTLING (*Zeitsch. "Technikern,"* 1916, Jan.; from *Chem. Zentr.*, 1921, iii, 106).—By reduction of campholide (see preceding abstracts), 1 : 2 : 2-trimethyl-1 : 3-dimethanol*cyclo*butane is obtained according to the equation,

$$\begin{array}{l} CH_2{-}CH{-}CH_2 \\ \;|\quad\;\; | \qquad\; \searrow \\ \;|\quad CMe_2 \quad O+4H= \\ \;|\quad\;\; | \qquad\; \nearrow \\ CH_2{-}CMe{-}CO \end{array} \qquad \begin{array}{l} CH_2{-}CH{-}CH_2{\cdot}OH \\ \;|\quad\;\; | \\ \;|\quad CMe_2 \\ \;|\quad\;\; | \\ CH_2{-}CMe{-}CH_2{\cdot}OH \end{array}$$

Oxidation of the glycol gives *d*-camphoric acid; it has $[\alpha]_D^{20}+64{\cdot}07°$ (in alcohol). The inner oxide, formed by the elimination of water, gives $[\alpha]_D^{20}+27{\cdot}20°$ (in ether). The corresponding dibromide was prepared, but not in a state of purity. G. W. R.

Action of Magnesium Phenyl Haloids on Diphenylchloroacetyl Chloride. Constitution of Triphenylvinyl Alcohol. ALEX. MCKENZIE and JOHN SCOTT WALKER BOYLE (T., 1921, **119**, 1131—1140).

A Compound of Sulphuric Acid with the Chloride and Anhydride of Benzoic Acid. MAX BERGMANN and FRITZ RADT (*Ber.*, 1921, **54**, [*B*], 1652—1655).—Benzoyl chloride combines readily with anhydrous sulphuric acid in chloroform solution to yield the *additive product*, $C_7H_7O_5ClS$, long, prismatic needles, m. p. 52—53° after previous softening. It may be preserved unchanged for some days in an absolutely dry atmosphere, but is very sensitive to atmospheric moisture and is immediately decomposed by water with the formation of benzoic acid, its activity in this respect far exceeding that of benzoyl chloride. The substance is dissociated easily into its components, and therefore yields benzoyl chloride and chlorosulphonic acid when treated with phosphorus pentachloride in the cold. Similarly, benzoic anhydride and sulphuric acid unite when dissolved in carbon disulphide to yield the *substance* $C_{14}H_{12}O_7S$, colourless needles or prisms, m. p. 70—72°. By analogy, these observations are considered to cast some doubt on the assumption that acetylsulphuric acid, $CH_3{\cdot}CO{\cdot}SO_4H$, is the active catalyst in acetylating mixtures of sulphuric acid and acetic anhydride. H. W.

Action of Methyl and Ethyl Alcohols on Esters of 2 : 6-Dinitro- and 2 : 4 : 6-Trinitro-benzoic Acids. J. J. SUDBOROUGH and D. D. KARVÉ (*J. Ind. Inst. Sci.*, 1921, **4**, 177—180).—The remarkable observation of Rosanoff and Prager (A., 1909, ii, 32) that 2 : 4 : 6-trichloro- or tribromo-benzoic acid is almost quantitatively esterified when heated with ethyl alcohol at 180—200° has led the authors to examine the possibility of alcoholysis under similar conditions with substances which might be expected to exhibit marked steric hindrance. It is found that methyl and

ethyl 2 : 6-dinitrobenzoates and methyl 2 : 4 : 6-trinitrobenzoate react with ethyl alcohol at about 180° with elimination of the carbalkyloxy-group and formation of the corresponding nitro-hydrocarbon. H. W.

Sulphonations in the Presence of Iodine. V. AUGER and (MLLE) M. VARY (*Compt. rend.*, 1921, **173**, 239—240).—Contrary to the results of Rây and Dey (T., 1920, **117**, 1405), the authors find that the sulphonation of benzoic acid either with or without the presence of iodine yields only 1% of *o*-sulphobenzoic acid. Similarly, in the sulphonation of catechol in the presence of iodine the authors obtained the 3-sulphonic acid mixed with some 3 : 4-di-sulphonic acid. Dihydroxybenzene-3-sulphonic acid gives a *basic barium* salt, $(C_6H_4O_2{\cdot}SO_3Ba)_2Ba,4H_2O$. The authors doubt the influence of iodine in sulphonations, which is attributed to it by Rây and Dey (*loc. cit.*). W. G.

Alcoholysis. IV. Alcoholysis of Esters of αβ-Unsaturated Acids and of the Corresponding Saturated Esters. B. DASANNACHARYA and J. J. SUDBOROUGH (*J. Ind. Inst. Sci.*, 1921, **4**, 181—203).—According to Sudborough and his co-workers (T., 1905, **87**, 1842; 1907, **91**, 1033; 1909, **95**, 315), an acid containing an αβ-unsaturated linking is esterified far more slowly than its saturated analogue when the catalytic method of esterification is used, whilst Williams and Sudborough (T., 1912, **101**, 412) have shown that the ethyl esters of αβ-unsaturated acids are hydrolysed much more slowly than the esters of the corresponding saturated acids. Since the processes of catalytic esterification and alcoholysis under the influence of hydrogen chloride have been shown to be similar in many respects, the authors have investigated the effect of an αβ-unsaturated linking in the acyl portion of an ester on alcoholysis, using hydrogen chloride as catalyst. The action of ethyl alcohol on methyl butyrate, methyl crotonate, methyl β-phenylpropionate, and methyl cinnamate and the corresponding reverse changes have been examined by a dilatometric method very similar to that used by Kolhatkar (T., 1915, **107**, 921). It is found that esters containing an αβ-olefinic linking in the acyl group undergo alcoholysis far less readily than the esters of the corresponding saturated acids, but that the effect is not so great as in esterification. A diminution of the alcoholysis constant is caused by the replacement of a β-methyl group by phenyl. Kolhatkar's generalisation (*loc. cit.*) that in the case of alcoholysis the ratio of the constants for the direct and the reverse reactions is roughly independent of the nature of the acyl group is confirmed.
H. W.

Hydrogenation of Aromatic Compounds by the Aid of Platinum. V. Hydrogenated Phenylnaphthylmethane-carboxylic Acids. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 1921, **54**, [*B*], 1420—1430; cf. this vol., ii, 185).—The shortage of fatty acids in Germany has led the authors to examine the possibilities of hydrogenated derivatives of *o*-benzoyl-

and *o*-naphthoyl-benzoic acids in this direction. It is found with these substances that the nucleus is first hydrogenated and the ketonic group is reduced subsequently. Also, hydrogenation follows a different course from that in the cases of benzene or naphthalene, since it is here possible to isolate incompletely hydrogenated products. The alkaline earth and heavy metal salts of perhydronaphthylmethylbenzoic acid are characterised by solubility in hydrocarbons, whilst the alkali salts are soaps corresponding, in this respect, with fatty acids containing about ten carbon atoms.

The possibilities of optical and geometrical isomerism of the perhydronaphthylmethylbenzoic acids are fully discussed and the isolation of four isomerides is described.

*Di*cyclo*hexylacetic acid*, rhombic platelets, m. p. 137°, is readily obtained by the hydrogenation of diphenylacetic acid in the presence of platinum; the *sodium*, *potassium*, *copper*, *ferric*, *silver*, and *lead* salts are described. Hydrogenation of *o*-benzylbenzoic acid in the presence of platinum charged with oxygen leads directly to the corresponding *perhydro-acid*, $C_6H_{11}\cdot CH_2\cdot C_6H_{10}\cdot CO_2H$, a viscous liquid which probably consists of a mixture of *cis-trans*-isomerides; the *potassium*, *calcium*, *lead*, *copper*, and *silver* salts are described. The first named of these does not behave as a soap.

α-Naphthoyl-*o*-benzoic acid, monoclinic sphenoidal crystals, $a:b:c=1{\cdot}565:1:1{\cdot}610$, $\beta=97°\ 54'$, m. p. 174°, is formed together with the corresponding β-naphthyl derivative by the action of phthalic anhydride on naphthalene in benzene solution in the presence of aluminium chloride; it is reduced by zinc dust in ammoniacal solution containing copper salts to *α-naphthylmethyl-o-benzoic acid*, $C_{10}N_7\cdot CH_2\cdot C_6H_4\cdot CO_2H$, triclinic crystals, m. p. 146°, the *sodium*, *calcium*, *barium*, *zinc*, *copper*, *iron*, *lead*, and *silver* salts of which were examined. When subjected to catalytic hydrogenation it gives as intermediate product, a *dihydro-acid*, $C_{18}H_{16}O_2$, long, thin, triclinic prisms, m. p. 163°, $a:b:c=0{\cdot}7311:1:0{\cdot}5161$; $\alpha=108°\ 54'$, $\beta=105°\ 44'$, $\gamma=93°\ 19'$ (the *sodium*, *lead*, *copper*, *calcium*, and *silver* salts are described). [α-Naphthoyl-*o*-benzoic acid in similar manner gives a *dihydro-acid*, $C_{18}H_{14}O_3$, in which the ketonic group remains intact; it crystallises in rectangular plates, m. p. 201°.] α-Naphthylmethyl-*o*-benzoic acid, or, preferably, α-naphthoyl-*o*-benzoic acid, is catalytically hydrogenated in the presence of oxygenated platinum to a mixture of *perhydro-α-naphthylmethylbenzoic acids*, $C_{10}H_{17}\cdot CH_2\cdot C_6H_{10}\cdot CO_2H$, which can be separated into its components by crystallisation from light petroleum, thereby yielding: α-acid, triclinic, asymmetric crystals, $a:b:c=0{\cdot}9641:1:1{\cdot}0141$; $\alpha=106°\ 49'$, $\beta=110°\ 19'$, $\gamma=83°\ 51'$, m. p. 129°; β-acid, triclinic, asymmetric crystals, $a:b:c=0{\cdot}6102:1:0{\cdot}5519$; $\alpha=101°\ 24'$, $\beta=101°\ 52'$, $\gamma=90°\ 37'$, m. p. 114°; γ-acid, needles, m. p. 94°; δ-acid, m. p. 82—84°. The solubilities of these acids in light petroleum, acetic acid, and ethyl acetate respectively have been determined. The corresponding salts of the isomeric acids are very similar to one another; the *sodium*, *calcium*, *lead*, *copper*, and *silver* compounds are described.

H. W.

Pinabietic Acid, a Definite Resin Acid. I. Isolation and Purification. OSSIAN ASCHAN (*Annalen*, 1921, **424**, 117—133).—The less volatile fractions obtained on distilling pine oil in a current of superheated steam yield a solid substance, from which, by methods for the details of which the original should be consulted, a well-characterised, crystalline acid, $C_{20}H_{30}O_2$, can be separated. This acid apparently belongs to the abietic series, and is named *pinabietic acid.* When pure, it separates from methyl alcohol in small, truncated prisms, m. p. 182—183°. It forms a normal *sodium* salt, $C_{20}H_{29}O_2Na$, which may be precipitated from methyl alcoholic solution, and two *acid sodium* salts, $C_{20}H_{29}O_2Na,2C_{20}H_{30}O_2$ and $C_{20}H_{29}O_2Na,3C_{20}H_{30}O_2$. The latter is obtained as a porcelain-like mass when carbon dioxide is passed into an aqueous solution containing the normal sodium salt, and is made use of in the separation of pinabietic acid from the impurities which accompany it.

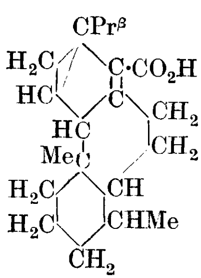
C. K. I.

Pinabietic Acid, a Definite Resin Acid. II. Molecular Weight and Rotatory Power. OSSIAN ASCHAN and K. E. EKHOLM (*Annalen*, 1921, **424**, 133—150).—Figures for the molecular weight of pinabietic acid, obtained both by titration and by the ebullioscopic method, using ether as solvent, agree closely with the value required for a monobasic acid having the formula $C_{20}H_{30}O_2$.

The remarkable influence of the nature of the solvent on the rotatory power of pinabietic acid appears to be a definite characteristic of that substance. Many of the measurements recorded in the paper were made before the method of purification (cf. preceding abstract) had been perfected, and, in consequence, were performed with specimens which were not absolutely pure. The numbers obtained, however, are quite accurate enough to indicate the general character of the effect under investigation, and the following measurements made with a specimen, m. p. 176—178°, are typical of a number which show that whilst in aromatic solvents pinabietic acid exhibits a strong dextrorotation, in aliphatic solvents it is lævorotatory: 2·60% solution in benzene $[\alpha]_D^{22°}$ +20·84°; 3·17% solution in ethyl alcohol $[\alpha]_D^{21°}$ −30·87°.

C. K. I.

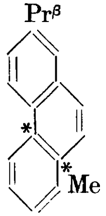
Pinabietic Acid, a Definite Resin Acid. III. Constitution of Pinabietic Acid. ARTTURI I. VIRTANEN (*Annalen*, 1921, **424**, 150—215).—With certain reservations, the annexed formula is held to express the constitution of pinabietic acid (cf. two preceding abstracts). This conclusion is drawn as the result of a fairly extensive study of the properties and decompositions of the substance.



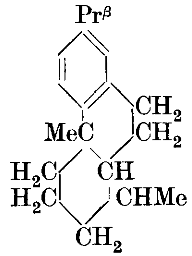
The investigation of the oxidation products of the substance was attended with difficulty. The only acid which could be isolated from the product

obtained using chromic acid mixture was acetic acid, but alkaline permanganate yielded *iso*butyric acid indicating (see below) the presence of an *iso*propyl group. The acid is certainly unsaturated not only towards permanganate but also towards all the usual reagents for the double bond. Thus with hydrogen bromide in glacial acetic acid at 0° a *dihydrobromide*, m. p. 188—192° (decomp.), is produced. This fact taken alone would seem to indicate that two double bonds are present, but hydrogen iodide forms only a *monohydriodide*, m. p. 191—193° (decomp.), bromine in carbon disulphide a *dibromide*, m. p. 107—110° (decomp.), and gaseous hydrogen in the presence of platinum black a *dihydro*-derivative, needles, m. p. 170—175°, all of which are fully saturated substances. The inference drawn from these observations is that pinabietic acid contains one double bond and one *cyclo*propane ring which undergoes fission with hydrogen bromide, but not with hydrogen iodide, bromine, or hydrogen and colloidal platinum. Determinations of the iodine number gave inconsistent results, but confirmation of the conclusion relating to the presence of the *cyclo*propane ring was derived from a study of the refractivities of the methyl and ethyl esters. These esters, it should be noticed in passing, are very difficult to prepare by the ordinary method, and, when once formed, are by no means easily hydrolysed. The *methyl* ester, b. p. 225—226°/16 mm., d_4^{21} 1·0500, n_D^{21} 1·52685, best obtained by the action of methyl sulphate on the sodium salt of the acid, gives $[R]_D$ 92·582, which is close to the value calculated assuming one double bond and one *cyclo*propane ring. The *ethyl* ester, b. p. 241—242°/20 mm., d_4^{21} 1·0339, n_D^{21} 1·52129, prepared from the silver salt and ethyl iodide, gives $[R]_D$ 97·320. These numbers are also of importance inasmuch as they appear to disprove the existence in the molecule of pinabietic acid of an aromatic nucleus, and this in the face of evidence which might be taken to indicate its presence; for pinabietic acid can be nitrated and sulphonated. The *dinitro*-derivative is a well-characterised substance, m. p. 190—193°, $[\alpha]_D^{22°}$ (1·91% solution in acetone) +43·89°, forming crystalline *ammonium*, *sodium*, *calcium*, *barium*, and *silver* salts, a *methyl* ester, m. p. 180—183°, and an *ethyl* ester, m. p. 160—162°, $[\alpha]_D^{23}$ (3·30% solution in acetone)+42·03°. On reducing the dinitro-acid with tin and hydrochloric acid a *diamino-acid* was formed and was isolated as its *dihydrochloride*, m. p. 280° (approx.).

When the chloride of pinabietic acid is distilled under reduced pressure, carbon monoxide and hydrogen chloride are evolved, and a hydrocarbon, $C_{19}H_{28}$, called *pinabietene*, b. p. 191—194°, $d_4^{20°}$ 0·9734, collects in the receiver. The same substance may be obtained by heating pinabietic acid in a sealed tube at 260—270°. It is quite stable towards cold permanganate, and undoubtedly contains an aromatic nucleus, as is shown by its behaviour on bromination, nitration, and sulphonation. The bromo- and nitro-derivatives were difficult to purify, but a definite *monosulphonic acid* was isolated in the form of its *calcium* salt. An important decomposition is that which takes place when pinabietene (or pinabietic acid) is heated with sulphur at 180—190°. Hydrogen



sulphide, and probably methyl mercaptan, are evolved, and *retene* (formula annexed) is produced, indicating that pinabietene is to be regarded as an octahydromethylretene, in which two of the three six-carbon rings are fully reduced. That the aromatic nucleus remaining is that which bears the *iso*propyl residue is clearly proved by the fact that pinabietene on oxidation, both by nitric acid and by manganese dioxide and sulphuric acid, yields trimellitic acid (benzene-1 : 2 : 4-tricarboxylic acid). The methyl group removed by heating with sulphur is presumably situated in one of the only two positions (marked by asterisks in the formula for retene), in which its elimination would be necessary to enable oxidation to an aromatic hydrocarbon to occur. No evidence has so far been forthcoming to enable this ambiguity to be resolved, but, excepting this, the annexed formula for pinabietene may be regarded as established.



It is clear from what precedes that the ring which in pinabietene has an aromatic character in pinabietic acid contains a double bond, a cross-linking similar to that present in thujene, and the carboxyl group, the elimination of which as $CO+H_2O$ causes reversion to the benzenoid form. The exact relation between these features and the remainder of the molecule cannot be determined with certainty on the evidence available, but from the refractive indices of the esters and the extraordinary stability towards acids and alkalis of pinabietic acid, which may be fused with potassium hydroxide and boiled with 50% sulphuric acid without any change occurring, it is considered (*a*) that the double bond is endocyclic, (*b*) that pinabietic acid is an αβ-unsaturated acid, and (*c*) that the double bond and cross-linking are in "conjugation." These conclusions are embraced in the formula given at the commencement of this abstract, although several alternatives are obviously possible.

Moreover, the stability of pinabietic acid towards zinc and acetic acid, and even towards sodium and boiling amyl alcohol, is rather an unusual property for an αβ-unsaturated acid.

The following physical constants are recorded for pure *pinabietic acid*: m. p. 182°, b. p. 255—257°/16 mm., $[\alpha]_D^{20^\circ}-30{\cdot}66^\circ$. On exposure to air, the m. p. is depressed, small amounts of resinous substances being produced. The *ammonium* salt is gelatinous and the *silver* salt amorphous, but the *calcium*, *strontium* ($7H_2O$), *barium* (H_2O), *lead*, and *copper* salts are crystalline.

In view of the extraordinary variations in the rotatory power of pinabietic acid in different solvents (cf. preceding abstract), the methyl and ethyl esters have now been examined in this connexion. In both cases qualitatively similar differences are observed, although the numerical values are not so large. The following are typical measurements: Methyl ester, 5·53% solution in methyl alcohol, $[\alpha]_D^{23^\circ}-4{\cdot}71^\circ$, 1·92% solution in benzene, $[\alpha]_D^{23^\circ}+14{\cdot}85^\circ$. Ethyl ester, 2·84% solution in ethyl alcohol, $[\alpha]_D^{20^\circ}-7{\cdot}77^\circ$, 2·73%

solution in benzene, $[\alpha]_D^{20}+12\cdot48°$. Both esters appear to possess normal molecular weights in benzene as well as in aliphatic solvents.

The author thinks it probable that Johansson's abietic acid (A., 1920, i, 232) was an impure form of pinabietic acid. He gives a concise summary of the literature of the abietic acids. C. K. I.

Isomerism of Formylphenylacetic Esters. VI. Alkylation of Formylphenylacetic Ester. WILHELM WISLICENUS and ROBERT V. SCHRÖTTER (*Annalen*, 1921, **424**, 215—232).—In continuation of former work (A., 1920, i, 841), the authors show that ethyl formylphenylacetate may be alkylated on carbon or on oxygen according to the conditions employed, higher temperatures favouring the formation of the C-alkyl derivatives, which may also be obtained from the corresponding O-alkyl compounds by heating. The compounds of both types undergo hydrolytic fission on treatment with acids and alkalis in close analogy with the ketonic and acid modes of hydrolysis of ethyl acetoacetate and its derivatives.

Ethyl α-formyl-α-phenylpropionate (the C-methyl compound), b. p. 125—128°/15 mm., is the principal product of the action of methyl iodide on a boiling alcoholic solution of ethyl sodioformylphenylacetate, and is the sole product when the experiment is conducted in a sealed vessel at 120°. It quickly reddens a magenta solution decolorised by sulphurous acid, and yields 1 : 4-*diphenyl*-4-*methyl*-5-*pyrazolone*, pale yellow prisms, m. p. 57°, on heating with phenylhydrazine. When hydrolysed with alcoholic sodium hydroxide, it gives α-phenylpropionic acid, whilst with dilute sulphuric acid it yields an oily aldehyde, b. p. 203—205°, giving a phenylhydrazone, m. p. 128—129°, thought to be α-phenylpropaldehyde, although it was not identified with certainty. The C-methyl compound does not decolorise permanganate in acetone or bromine in chloroform in the cold (distinction from the O-methyl isomeride).

Ethyl phenylmethoxymethyleneacetate [β-methoxyatropate] (the O-methyl derivative), colourless prisms or needles, m. p. 54—55°, b. p. 173—174°/15 mm., is the chief product of the action at the ordinary temperature of methyl sulphate and aqueous sodium hydroxide on ethyl formylphenylacetate, and is the sole product if the decomposition be carried out at 0°. It reddens decolorised magenta only slowly, but instantly decolorises cold permanganate, and can be titrated with a chloroform solution of bromine (distinction from the C-methyl compound). In the last reaction, two atoms of bromine are taken up, but are liberated again on evaporating the solvent, pure ethyl β-methoxyatropate remaining. On hydrolysis by means of alcoholic sodium hydroxide, the O-methyl compound yields phenylacetic acid and formic acid, whilst with dilute sulphuric acid it gives phenylacetaldehyde and carbon dioxide. It does not pass into the C-methyl derivative on repeated distillation under diminished pressure, but is completely converted at 240°.

The action of methyl sulphate at temperatures higher than that

of the atmosphere leads to the formation of considerable quantities of the C-methyl compound. When, for example, it is allowed to act on a suspension in boiling benzene of dry ethyl sodioformylphenylacetate a mixture of approximately equal quantities of the two isomerides is produced, whilst with ethyl formylphenylacetate and warm 30% aqueous potassium hydroxide the product obtained is ethyl α-phenylpropionate, evidently derived from the C-methyl compound by hydrolysis.

*Ethyl α-formyl-α-phenyl-*n*-butyrate*, b. p. 125—127°/12 mm., and *ethyl β-ethoxyatropate*, b. p. 174—175°/12 mm. (the C- and O-ethyl derivatives), are generally very similar in their modes of formation and properties to the corresponding methyl compounds, although the C-ethyl derivative is formed in rather greater proportion than the C-methyl compound under similar experimental conditions. Moreover, the conversion of ethyl β-ethoxyatropate into ethyl α-formyl-α-phenyl-*n*-butyrate takes place at a lower temperature than is the case with the methyl compounds, and may be brought about by repeated distillation under diminished pressure. Again, *ethyl α-formyl-αβ-diphenylpropionate*, a strongly odorous oil, b. p. 184—185°/17 mm., is the only compound which can be isolated by distillation from the product of the action of benzyl chloride on alcoholic ethyl sodioformylphenylacetate, although, to judge by the action on bromine in chloroform solution of the undistilled oil, a certain amount of the O-benzyl ether must have been formed originally.

Ethyl sodioformylphenylacetate reacts with ethyl bromoacetate, giving *ethyl α-formyl-α-phenylsuccinate*, a viscous oil, b. p. 203—205°/12 mm., and with ethyl chloroformate yielding *ethyl β-ethylcarbonatoatropate*, $CO_2Et\cdot O\cdot CH{:}CPh\cdot CO_2Et$, a viscous oil, b. p. 199°/15 mm., giving the reactions characteristic of unsaturated compounds. C. K. I.

The Two Methyl *d*-Allylcamphorcarboxylates, the Three Propan-β-olcamphorcarboxylolides, and the Camphopropan-β-ol which is derived from them. A. HALLER and (MME) RAMART-LUCAS (*Compt. rend.*, 1921, **173**, 115—120; cf. A., 1903, i, 503).—In the preparation of the methyl *d*-allylcamphorcarboxylates two stereoisomerides are obtained, one of which is solid, m. p. 75—76° and the other liquid, but never entirely free from the solid form. The solid isomeride has a much lower specific rotatory power than the liquid and in either case the value of $[\alpha]_D$ is less in solution in benzene than in alcohol. The solid methyl allylcamphorcarboxylate, when treated with strong sulphuric acid, gives two isomeric propan-β-olcamphorcarboxylolides, one m. p. 141° and the other m. p. 89—90°. The liquid ester gives a *camphorcarboxylolide*, m. p. 117—118° isomeric with the other two. The two camphorcarboxylolides, m. p. 141° and 117—118°, when heated with alcoholic potassium hydroxide, give the same *camphopropan-β-ol*, $C_8H_{14}{<}{\overset{CH\cdot CH_2\cdot CHMe\cdot OH}{\underset{CO}{|}}}$, b. p. 162—164°/14 mm.; $[\alpha]_D +31° 25'$, giving a *phenylurethane*, m. p. 116—117°; $[\alpha]_D +45° 4'$. W. G.

The Esterification of Dimethylamino*iso*phthalic Acid. II. Preparation of 4-Dimethylamino*iso*phthalic Acid. III. Esterification of 4-Dimethylamino*iso*phthalic Acid. N. SMODLAKA (*Rev. Chim.*, 1921, **1**, 88—101; cf. A., 1920, i, 737, and this vol., i, 418).—Methyl 4-amino*iso*phthalate is converted by means of methyl sulphate successively into *methyl* 4-*methylamino*iso*phthalate*, m. p. 115°, and methyl 4-dimethylamino*iso*phthalate, both of which yield the corresponding acids on hydrolysis with alcoholic potassium hydroxide.

The work described in the second paper (III) has already been published (see A., 1920, i, 737). C. K. I.

Additional Properties of the Keto-enolic Double Linking. H. GAULT and R. WEICK (*Compt. rend.*, 1921, **173**, 315—318; cf. A., 1920, i, 485, 675).—The β-form of ethyl phenylpyruvate is converted by hydrogen chloride or bromide into the α-isomeride, but with hydrogen iodide it undergoes hydrogenation. If ammonia is bubbled through the liquid β-ester, it is converted into *phenylbenzylbutyrolactonecarboxylamide*, m. p. 229°. If the ester is first dissolved in ether and ammonia passed into this solution at −15°, four compounds are obtained. The first *compound* is only stable at −15° and loses ammonia when the temperature rises. The second is the amide described above. The third is *ethyl phenylbutyrolactonecarboxylate*, m. p. 140°, and the fourth is the *ammonium* salt corresponding with the enolic form of this ester. If ammonia is replaced by diethylamine in this reaction, the only product is the *diethylamine* salt, m. p. 130—135°, of ethyl phenylbutyrolactonecarboxylate. W. G.

An Ammonium Molybdoquinate. GEORGES TANRET (*Compt. rend.*, 1921, **173**, 43—45).—The author has isolated a crystalline *ammonium quinomolybdate* having the constitution

$$OH{\cdot}MoO_2{\cdot}O{\cdot}C_7H_{10}O_5{\cdot}NH_4,aq.$$

and $[\alpha]_D -22{\cdot}5°$ (in nitric acid). If an excess of ammonium molybdate is mixed with a solution of quinic acid, there is evidence of the formation of another compound, not isolated, having $[\alpha]_D -72°$. W. G.

The Formation and Stability of *spiro*-Compounds. VI. New Derivatives of *cyclo*Propane and *cyclo*Hexane*spirocyclo*propane. STANLEY FRANCIS BIRCH, WILLIAM HENRY GOUGH, and GEORGE ARMAND ROBERT KON (T., 1921, **119**, 1315—1328).

The Reagent "Iodine+Alkali." Action on some Organic Nitrogenous Compounds. PAUL ROBIN (*Ann. Chim.*, 1921, [ix], **16**, 77—140).—A more detailed account of work already published (cf. A., 1919, i, 489, 592; 1920, i, 95, 568; this vol., i, 113, 272). W. G.

A New Case of Anisotropy in Melting Point. ARNO MÜLLER (*Ber.*, 1921, **54**, [*B*], 1481—1482).—Dianisylidene*cyclo*hexanone (cf. Wallach, A., 1907, i, 220), prepared by the action of aqueous sodium hydroxide on a mixture of *cyclo*hexanone and anisaldehyde, melts

completely at 160—161° to a cloudy liquid, which suddenly becomes transparent at 171°; it is very well adapted for the experimental demonstration of anisotropy. H. W.

Benzylidenecarvone. ARNO MÜLLER (*Ber.*, 1921, **54**, [*B*], 1471—1481).—Under certain definite conditions it has been found possible to prepare benzylidenecarvone and to separate it into a liquid (α) and a solid (β) modification. Comparison of the ultra-violet absorption spectra of these substances with those of benzylidenedihydrocarvone and benzylidenementhone shows close similarity in the cases of the α-form and benzylidenedihydrocarvone and the β-form and benzylidenementhone. β-Benzylidenecarvone must therefore have the formula $CMe{<}{\begin{matrix}CO\cdot C(CHPh)\\ CH\text{——}CH_2\end{matrix}}{>}CH\cdot CMe{:}CH_2$, whilst that of the α-variety cannot yet be decided with certainty.

Sodium hydroxide solution (15%) is gradually added to a solution of benzaldehyde and carvone (d^{15} 0·9642, $[\alpha]_D$ −59·48°) in alcohol, care being taken that the temperature does not exceed +2° to +3°, and the mixture is subsequently preserved at the atmospheric temperature during forty-eight hours. The product is fractionated repeatedly under diminished pressure, thereby giving a mixture of benzylidenecarvones from which, after some time, the β-form crystallises. β-*Benzylidenecarvone* forms almost colourless leaflets, m. p. 114—115°, $[\alpha]_D$ −815° in ethyl alcoholic solution, whereas the α-*derivative* (which was possibly not quite homogeneous) is a pale yellow oil which shows no tendency to crystallise, b. p. 191—193°/10 mm., d^{15} 1·041, $[\alpha]_D$ +152·30°. Attempts to convert either form into an oxime or a semicarbazone were unsuccessful. The α-variety absorbs hydrogen chloride in dry ethereal solution with the formation of an unstable, dark brown oil, whereas the β-form remains unchanged when treated similarly.

Benzylidenedihydrocarvone is reduced by sodium to benzylidenedihydrocarveol, b. p. 182—184°/11 mm. (*phenylurethane*, m. p. 233—234°). The same phenylurethane is prepared from the product of the reduction of α- or β-benzylidenecarvone by sodium in alcoholic solution. Oxidation of α- or β-benzylidenecarvone by potassium permanganate yields mainly benzoic acid.

Benzylidenementhone, b. p. 182—183°/8 mm., is conveniently prepared by saturating a mixture of its components with hydrogen chloride. H. W.

Course of the Reduction of Benzylidenediacetylmonoxime and the Preparation of Benzyldiacetyl. OTTO DIELS and WALTER POETSCH (*Ber.*, 1921, **54**, [*B*], 1585—1591).—Reduction of benzylidenediacetylmonoxime, $CHPh{:}CH\cdot C(N\cdot OH)\cdot COMe$, by aluminium amalgam in boiling alcoholic solution gives a mixture of products from which α-*phenylpentane*-δ-*one*, a colourless, mobile liquid with a pleasant odour, b. p. 105—110°/2 mm., has been isolated (*semicarbazone*, lustrous leaflets, m. p. 125°). It is transformed by amyl nitrite and hydrochloric acid into *benzyldiacetylmonoxime*, $CH_2Ph\cdot CH_2\cdot C(N\cdot OH)\cdot COMe$, long, matted needles, m. p.

93°. Catalytic reduction of benzylidenediacetylmonoxime in the presence of platinum does not give satisfactory results, and hydrogen is only slowly absorbed; with palladium, on the other hand, reduction is rapid, and the end point is sharply defined. A mixture of substances is produced from which it has been found possible to isolate 3 : 6-*di*-β-*phenylethyl*-2 : 5-*dimethylpyrazine*,

$$CH_2Ph\cdot CH_2\cdot C{<}{}^{CMe=N}_{N-CMe}{>}C\cdot CH_2\cdot CH_2Ph,$$

slender, colourless needles, m. p. 104°, and benzyldiacetylmonoxime (see above). The latter gives a *phenylhydrazone*, pale yellow needles, m. p. 149°, and a *dioxime*, colourless leaflets, which is transformed by nitrogen peroxide in dry ethereal solution into the *furoxan*, $C_{11}H_{12}O_2N_2$, coarse, pearly crystals, m. p. 63—64°. Benzyldiacetylmonoxime is converted by boiling sulphuric acid (35%) into *benzyldiacetyl*, $CH_2Ph\cdot CH_2\cdot CO\cdot COMe$, b. p. 128—129°/19 mm.

H. W.

The Formation and Stability of *spiro*-Compounds. V. Derivatives of *cyclo*Hexane*spirocyclo*hexane and of *cyclo*-Pentane*spirocyclo*hexane. WOODFORD STANLEY GOWAN PLUCKNETTE NORRIS and JOCELYN FIELD THORPE (T., 1921, **119**, 1199—1210).

Anthraquinone and its Derivatives as Reductive Catalysts. CHARLES SUNDER and MARCEL BADER (*Bull. Soc. Ind. Mulhouse*, 1921, **87**, 187—189).—The facility with which anthraquinone is reduced to anthraquinol and the ready oxidisability of the latter render it an excellent hydrogen carrier for the hydrogenation of difficultly reducible substances such as α-naphthaleneazo-β-naphthol. This property is not exhibited to the same extent by a considerable number of derivatives of anthraquinone which have been examined; on the other hand, 2-hydroxyanthraquinone is somewhat more active than the parent substance.

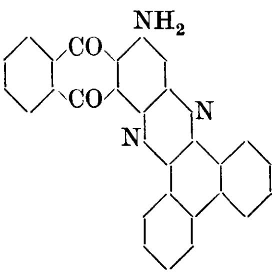
H. W.

Certain Nitroamines of the Anthraquinone Series. ERNST TERRES (*Monatsh.*, 1920, **41**, 603—612).—The work of Scholl (A., 1905, i, 70) and of Scholl and Krieger (A., 1905, i, 145) is continued.

Nitro-1-*nitroaminoanthraquinone*, $C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2(NO_2)\cdot NH\cdot NO_2$, prepared by the action of nitric acid (*d* 1·5) on 1-aminoanthraquinone, forms a pale brown precipitate, exploding at 149—151°, or, if heated more slowly, at 10—15° lower; the position of the nuclear nitro-group was not ascertained.

2 : 4-*Dinitro*-1-*nitroaminoanthraquinone*, $C_{14}H_6O_8N_4$, formed along with the previous compound, separates in pale yellow crystals, exploding at 137—142°, or slowly decomposing at 100°. By alkali hydroxides or ammonia in the cold, or by sodium acetate solution in the hot, it is converted into the salts of the *aci*-form, these being difficultly soluble in cold, but readily so in hot, water, which, however, hydrolyses them rapidly. Aniline dissolves the nitroamine, giving a reddish-brown salt, and at above 100° the

solution becomes bluish-green, apparently owing to the formation of compounds similar to those formed from aniline and 2 : 6-dibromo-4 : 8-dinitro-1 : 5-dinitroaminoanthraquinone (Scholl and Krieger, *loc. cit.*). Treatment by the ordinary denitrating media, for instance, phenol and sulphuric acid, converts the nitroamine into 2 : 4-dinitro-1-aminoanthraquinone, m. p. 270—272° (uncorr.); the latter is reduced by ammonium sulphide to 1 : 2 : 4-triaminoanthraquinone (cf. D.R.-P. 264290, A., 1914, i, 63), which forms a bluish-red powder, remaining unmelted at 300°, and dissolves in acetic acid to a violet-red solution (1 : 2-diaminoanthraquinone-red), in concentrated sulphuric acid to a reddish-brown solution with a blue tinge, and in alkaline sodium hyposulphite solution to a brownish-red dye, showing scarcely any affinity for unmordanted vegetable fibres.



As an ortho-diamino-compound, 1 : 2 : 4-triaminoanthraquinone reacts readily with *o*-diketones; by phenanthraquinone in acetic acid it is converted into 4-*amino*-1 : 2-(9′ : 10′)*phenanthrazinoanthraquinone* (annexed formula), which is obtained as a mass of brown crystals.

Dinitro-1 : 5-*dinitroaminoanthraquinone*, $C_{14}H_6O_{10}N_6$, prepared by the nitration of 1 : 5-diaminoanthraquinone, forms a greenish-yellow, crystalline powder, exploding at 121—122°, or, if heated slowly, decomposing gradually from 116° upwards; it behaves towards alkalis, sodium acetate, or aniline similarly to 2 : 4-dinitro-1-nitroaminoanthraquinone. Treatment with phenol and sulphuric acid converts it into *dinitro*-1 : 5-*diaminoanthraquinone*, $C_{14}H_8O_6N_4$, which forms as a deep red precipitate, and by acids is precipitated in red flocks from its solution in dilute sodium hydroxide. Reduction of this compound by means of ammonium sulphide results in the formation of 1 : 5 : ? : ?-*tetra-aminoanthraquinone*, $C_{14}H_{12}O_2N_4$, which forms a blue powder and is converted into a deep brown azine (?) by the action of phenanthraquinone in acetic acid solution.

T. H. P.

Synthesis of 1 : 6-Dihydroxy-2-methylanthraquinone. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (T., 1921, **119**, 1339—1348).

The Methyl-1 : 2-benzanthraquinone Series. III. R. SCHOLL, CHRISTIAN SEER, and ALOIS ZINKE (*Monatsh.*, 1921, **41**, 583—602; cf. Scholl and Tritsch, A., 1912, i, 36, Scholl and Neuberger, A., 1912, i, 562).—The preparation of 3-chloro-4-methyl-1 : 2-benzanthraquinone is described. Its constitution is deduced from its formation from 3-amino-4-methyl-1 : 2-benzanthraquinone (Scholl and Neuberger, *loc. cit.*) and also by its transformation under the influence of molten potassium hydroxide into 4-*methyl*-1 : 2-*benzanthraquinone*, brown needles, m. p. 215—216°, which is converted by the successive action of potassium

permanganate and boiling acetic anhydride into the anhydride of anthraquinone-1 : 2-dicarboxylic acid.

2-Chloro-1-methylnaphthalene, a pale yellow liquid, b. p. 144—145°/12 mm., 155°/23 mm., is prepared in the usual manner from 2-amino-1-methylnaphthalene hydrochloride and is converted by nitric acid (*d* 1·4) at 5° into a mixture of *mononitro*-derivatives, slender, pale yellow needles, m. p. 133—134°, and slender, yellow needles, m. p. 70—80°. With phthalic anhydride in the presence of aluminium chloride and carbon disulphide, it gives o-6-*chloro-5-methylnaphthoylbenzoic acid*, colourless prisms, m. p. 182°. The latter is transformed by sulphuric acid or by successive treatment with thionyl chloride and aluminium chloride into 3-*chloro*-4-*methyl*-1 : 2-*benzanthraquinone*, yellow or greenish-yellow needles, m. p. 268°. When impure specimens of this substance are treated with molten potassium hydroxide, a second *methylbenzanthraquinone*, yellowish-brown needles, m. p. 225—226°, is obtained.

α-Methoxynaphthalene and phthalic anhydride, under the influence of aluminium chloride and carbon disulphide, give a mixture of o-4-*methoxynaphthoylbenzoic acid*, small, yellow needles, m. p. 192—193° (the *sodium* and *calcium* salts are described), and o-4-*hydroxynaphthoylbenzoic acid*, long, slender, yellow needles, m. p. 206—208° (the *sodium* and *silver* salts were prepared).

α-Naphthoyl-*o*-benzoic acid is reduced by zinc dust in boiling alkaline solution to *phenyl-α-naphthylmethane-2′-carboxylic acid*, $C_{10}H_7·CH_2·C_6H_4·CO_2H$, colourless plates, m. p. 145—146°; it yields a *mononitro*-derivative when treated with nitric acid (*d* 1·52), acetic acid, acetic anhydride, and carbamide at 6°. H. W.

Optical Investigations in the Chemistry of the Terpenes. I. ARNO MÜLLER (*Ber.*, 1921, **54**, [*B*], 1466—1471).—The author has examined the absorption in the ultra-violet of citronellol, geraniol, and reuniol, their acetates, *cyclo*-products and *cyclo*-esters. The isolation of the former in the optically pure condition does not present any special difficulties; the *cyclo*-products and their derivatives are, however, less easy to purify, but do not present the same difficulties as the true terpenes. The absorption curve of reuniol and its acetate lies intermediately between those of citronellol and geraniol and their acetates. The curves of *cyclo*-citronellol, *cyclo*geraniol, and *cyclo*reuniol (prepared by treatment of their esters with phosphoric acid at a low temperature) lie so closely together that it is very probable that those of the completely purified alcohols would be identical with one another, but greater displacements are observed with the acetates. Dihydrocitronellol, hydrogenated reuniol, and tetrahydrogeraniol give practically identical curves. These results, considered in conjunction with the chemical characteristics, prove that reuniol is a mixture of citronellol and geraniol, containing at least 60% of the latter. The hydrogenated product must be 2 : 6-dimethyloctane-8-ol.

The following physical constants are recorded: citronellol (from Java oil of lemon), b. p. 112·5°/8 mm., d^{15} 0·8612, α_D^{20} 2° 16′; (from citronellal), b. p. 113·2°/8 mm., d^{15} 0·8600, α_D^{20} 4° 5′; citronellyl

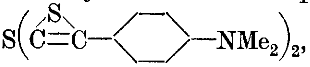
acetate, b. p. 117·3°/14 mm., d^{15} 0·8902, α_D^{20} 2° 6′; *cyclo*citronellol, b. p. 97—101°/8·5 mm., d^{15} 0·9023, α_D^{20} 2° 30′; *cyclo*citronellyl acetate, b. p. 108—111°/19 mm., d^{15} 0·9111, α_D^{20} 2° 31′; dihydrocitronellol, b. p. 113·5°/15 mm., d^{15} 0·8565; geraniol, b. p. 108·2°/9 mm., d^{15} 0·8836; geranyl acetate, b. p. 127·8°/14 mm., d^{15} 0·9123; *cyclo*geraniol, b. p. 96—98°/11 mm., d^{15} 0·9462; *cyclo*geranyl acetate, b. p. 103—107°/20 mm., d^{15} 0·9432; tetrahydrogeraniol, b. p. 116—117·5°/14·5 mm., d^{15} 0·8621. H. W.

Volatile Oil from Leaves of *Ocimum Gratissimum*, Linn. O. D. ROBERTS (*J. Soc. Chem. Ind.*, 1921, **40**, 164T—165T).—A sample of oil from *Ocimum Gratissimum*, Linn., originating from Seychelles, contained 16·0% terpenes (chiefly ocimene; cf. van Romburgh, A., 1901, i, 220), 55·0% phenols (chiefly eugenol), 5·6% phenolic ethers (arbitrarily calculated as methylchavicole although no definite indication could be obtained of this compound), 13·0% alcohols (probably linalool), 0·6% esters (determined as $C_{10}H_{17}$·OH). These results are, on the whole, similar to those recorded by van Romburgh (A., 1909, i, 597) and Schimmel & Co. (A., 1908, i, 666), although the chief phenolic constituent observed by Roure-Bertrand Fils (A., 1913, i, 746) was thymol. J. K.

Composition of the Essential Oil of Aburachan. YEINOSUKE SHINOZAKI (*J. Chem. Ind. Japan*, 1921, **24**, 444—463).—By distillation of the leaves and twigs of aburachan, *Lindera præcox*, Bl., about 0·3% of a light brown oil of camphoraceous odour was obtained. The following substances were isolated as its chief constituents: α-pinene, camphene, cineole, an aliphatic terpene, perhaps $C_{10}H_{16}$, b. p. 40—41°/2 mm., d^{15} 0·8251, borneol (both free and in combination), geraniol, caryophyllene, *d*-cadinene, a *sesquiterpene alcohol*, $C_{15}H_{26}O$, b. p. 140—142°/4 mm., d^{15} 0·974, n^{20} 1·5072, α −5° (this on treatment with phosphoric oxide yielded a bicyclic *sesquiterpene*, b. p. 101—103°/1·5 mm., d^{15} 0·9243, n^{20} 1·510), acetic acid (as ester), a decenoic acid (as ester), $C_{10}H_{18}O_2$, b. p. 106—107°/1·5 mm., which is probably identical with citronellic acid, and a weak, saturated acid having a high b. p. [See, further, *J. Soc. Chem. Ind.*, 1921, September.] K. K.

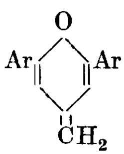
Constituents of Fir Tree Resin (Turpentine from *Pinus sylvestris*). F. HENRICH (*Zeitsch. angew. Chem.*, 1921, **34**, 363—367).—When distilled with steam the resin yielded from 22 to 24% of turpentine; the latter had b. p. 155—161° and $[\alpha]_D^{20}$ +11·32°. Saponification removed small amounts of free acids and esters, and the residual oil consisted of pure terpenes; α- and β-pinene were present. The non-volatile portion of the resin had m. p. 120—125°; acid number 167; ester number 3·4 to 14·1; $[\alpha]_D^{20}$ −44° (in alcohol solution). W. P. S.

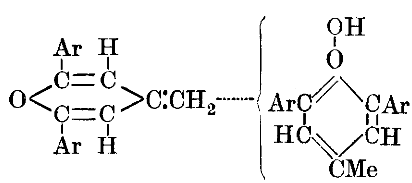
Synthesis of Basic Colouring Matters by the Condensation of Acetylene with Aromatic Bases. F. CONSONNO and A. CRUTO (*Gazzetta*, 1921, **51**, i, 177—183).—When acetylene is passed into a solution of sulphur in aniline heated at 150°, dithio-oxanilide (cf. Wallach, A., 1880, 556; Holleman, A., 1894, i, 241) is

formed in a yield quantitative with respect to the aniline used, tetrathio-oxalic acid, $CS_2H{\cdot}CS_2H$, being probably formed as an intermediate product. If the aniline is replaced by dimethylaniline, two compounds result: (1) $C_{20}H_{20}N_2S_3$, probably , a brown powder, m. p. 153°, which seems to be formed by condensation of the dimethylaniline with the thioanhydride corresponding with tetrathio-oxalic acid, this being presumably formed as the initial product. (2) A *compound* which could not be crystallised and undergoes ready oxidation in the air, yielding methyl-violet; it is considered to have the constitution, $C(C_6H_4{\cdot}NMe_2)_3{\cdot}C(C_6H_4{\cdot}NMe_2)_3$. Similarly, by the action of acetylene on sulphur and phenyl-α-naphthylamine and condensation of the product with excess of dimethylaniline, Victoria-blue is formed.

T. H. P.

Pyranhydrones, a New Group of Coloured, Quinhydrone-like Additive Compounds. WILHELM SCHNEIDER and HEINRICH F. W. MEYER (*Ber.*, 1921, **54**, [*B*], 1484—1503).—The action of a mixture of acetic anhydride and concentrated sulphuric acid on alkaloids has been investigated repeatedly and has been found to lead uniformly to the introduction of the acetyl group in the para-position to the oxygen atom of the phenolic ether. The behaviour of simpler phenolic ethers has now been examined, and is shown to lead to the primary production of methyl ketones of the ethers, which readily undergo further change with the production of unstable coloured substances, the properties of which closely resemble those of oxonium salts. By the addition of perchloric acid, the isolation of the sparingly soluble 4-methyl-2 : 6-diarylpyrylium perchlorates has been accomplished, and the salts are shown to be identical with those described recently by Dilthey. These salts, when treated with alkali, give bluish-violet products which are formed by the loss of a molecule of water from two molecules of the oxonium base (or ψ-base) of the pyrylium salts. The alteration in colour of these solutions caused by change in temperature indicates that the substances are constituted similarly to the quinhydrones. Their mode of formation is considered to be as follows. The pyrylium salt is converted by weak alkali into the oxonium base, which subsequently undergoes transformation into the ψ-base, from which a γ-methylenepyran (annexed formula) is derived by loss of water; the latter, in virtue of the residual affinity of the carbon atom of the semicyclic group unites with a molecule of non-dehydrated oxonium or ψ-base with the formation of a coloured product for which the general name "pyranhydrone" is proposed and to which the annexed formula is ascribed.





[In part with KURT VOLLRATH].—Acetophenone is converted by treatment with acetic anhydride and sulphuric acid, dilution of the mixture with water and subsequent addition of perchloric acid into 2 : 6-*diphenyl*-4-*methylpyrylium perchlorate*, coarse, yellow plates, m. p. 250—260°, according to the rate of heating; the corresponding *picrate* crystallises in brownish-red plates, m. p. 155°. The constitution of the compound is deduced from the identity of the substance produced by treating it with ferric chloride and concentrated hydrochloric acid with the compound described by Dilthey (A., 1916, i, 829). 2 : 6-*Diphenyl*-4-*methylpyranhydrone*, $C_{18}H_{16}O_2,C_{18}H_{14}O$, is prepared by treatment of the product of acetylation of acetophenone with water and ether and cautious addition of the aqueous liquid to a solution of sodium acetate; it is a fine, amorphous, violet powder, which softens at 55°, melts indistinctly at 90°, and decomposes at a higher temperature. It is soluble in the majority of organic solvents with the formation of unstable violet solutions which gradually become dirty brown. The solutions become lighter in colour when warmed, but on cooling return to their original colour, which increases in intensity when the solutions are placed in a mixture of carbon dioxide and ether. It loses a molecule of water when heated in a high vacuum at 125°, and yields a brownish-black, glassy *anhydro-substance* which has the composition $C_{18}H_{14}O$, but probably consists of a polymeride; it dissolves in organic media with the production of the dirty brown solutions characteristic of discoloured solutions of the original compound. Its re-conversion into the pyranhydrone or a pyrylium salt has not yet been effected. Under the influence of acids, the pyranhydrone becomes converted into the corresponding pyrylium salt, and a greyish-green, amorphous, neutral *substance*, which appears to have the composition $C_{36}H_{30}O_3$; this compound evolves water when heated in a high vacuum.

Anisole is converted by short treatment with acetic anhydride and sulphuric acid into *p*-methoxyacetophenone, m. p. 37—38°, b. p. 265°/750 mm., 108°/0·003 mm. More protracted treatment with the mixture and subsequent addition of perchloric acid gives 2 : 6-*di*-p-*anisyl*-4-*methylpyrylium perchlorate*, a brown or orange-red, crystalline powder, m. p. 245° (decomp.) [*picrate*, brownish-red powder, m. p. 185°]. 2 : 6-*Di*-p-*anisyl*-4-*methylpyranhydrone*, $C_{20}H_{20}O_4,C_{20}H_{18}O_3$, prepared in the same manner as the corresponding compound from acetophenone, is a dark violet, amorphous powder which shrinks together at 50°, melts indefinitely at about 80°, and decomposes at a higher temperature. In solution it behaves in precisely the same manner as the acetophenone derivative. When dehydrated in a high vacuum at 125°, it gives an *anhydro-product*, $C_{20}H_{18}O_3$. It is converted by acids into the corresponding pyrylium salt and a brown, amorphous, neutral material.

Attempts to prepare the pyrylium chloride led to the isolation of a basic *salt*, $C_{20}H_{19}O_3Cl,C_{20}H_{20}O_4$, a yellowish-orange, crystalline powder, m. p. 198°. H. W.

Iodine as a Catalyst in the Preparation of Coumarin. HIDEKICHI YANAGISAWA and HAJIME KONDÔ (*J. Pharm. Soc. Japan*, 1921, No. **472**, 498—502).—In the preparation of coumarin by Perkin's method, a good yield is obtained by the use of iodine as catalyst. Ninety grams of salicylaldehyde, 120 grams of acetic anhydride, 150 grams of sodium acetate, and 2 grams of iodine are boiled for two hours at 120°, and then for four hours at 180—195° under reflux, the resulting product is poured into cold water, and the coumarin extracted with ether. The yield was 70%; using 25 grams of zinc chloride as catalyst only 49% was obtained, whilst without any catalyst the yield fell to 27%. K. K.

Formation of Flavones and Benzylidenecoumaranones from Hydroxyphenyl Styryl Ketone Dibromides. KARL VON AUWERS and LUDWIG ANSCHÜTZ (*Ber.*, 1921, **54**, [*B*], 1543—1560).—It has been shown previously that halogenated and unsaturated hydroxy-ketones of the types $OH\cdot C_6H_4\cdot CO\cdot CHBr\cdot CHRBr$ and $OH\cdot C_6H_4\cdot CO\cdot CH{:}CHR$ readily yield substances containing a new six-membered ring, whereas the formation of a five-membered ring occurs only to a minor extent. On the other hand, von Kostanecki and his co-workers have found that the bromides of *o*-acetoxyphenyl styryl ketones yield flavones or benzylidenecoumaranones according to the substituents in the benzene nucleus, and have endeavoured to trace a connexion between the production of a five- or six-membered ring and the stability of the acetyl group; if this is first removed, a flavone results from the hydroxyphenyl styryl ketone dibromide, whilst if the hydrogen bromide and acetic acid are eliminated in the given order a benzylidenecoumaranone results. Further experiment, however, has proved that this explanation is inadequate, since it has been found possible to transform a hydroxyphenyl styryl ketone dibromide into a flavone or a coumaranone at will by suitable variation of the experimental conditions. It appears that during the action of alkali on the *o*-hydroxyphenyl styryl ketone dibromides two processes occur simultaneously, the relative velocities of which are dependent, in the first place, on external conditions, and, in the second place, on the substituents in the benzene nucleus.

o-Acetyl-*p*-cresol condenses with anisaldehyde in the presence of sodium hydroxide, giving a mixture of 4-*hydroxy*-m-*tolyl* 4-*methoxystyryl ketone*, $OH\cdot C_6H_3Me\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, long, pale yellow plates or orange needles, m. p. 98—99°, and minor amounts of 4′-*methoxy*-6-*methylflavanone*,

$$C_6H_3Me\begin{cases}CO-CH_2\\ O-\!\!-CH\cdot C_6H_4\cdot OMe\end{cases},$$

colourless, pearly leaflets, m. p. 110°. All attempts to isolate a possible intermediate alcohol, $OH\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot OMe$, were unsuccessful. The ketone gives an *acetate*, pale yellow, lustrous needles, m. p. 116°, a *dibromide*, pale yellow granules, m. p. 146° (decomp.), and the *acetate* of the dibromide, m. p. about 126—127°.

4′-*Methoxy*-6-*methylflavone*, $C_6H_3Me\begin{cases}CO-CH\\ O-\!\!-C\cdot C_6H_4\cdot OMe\end{cases}$, slender,

pale yellow, silky needles, m. p. 170°, is prepared in about 80% yield when aqueous sodium hydroxide solution is violently agitated with a suspension of the hydroxy- or acetoxy-ketone dibromide in alcohol; on the other hand, when the alkali is added to a boiling solution of either of these substances in alcohol, 5-*methyl*-4′-*methoxybenzylidenecoumaranone*,

$$C_6H_3Me{<}{}^{CO}_{O-}{>}C{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

slender, canary-yellow needles, m. p. 152°, is obtained in about 20% yield. Attempts to isolate intermediate compounds by the use of a smaller proportion of alkali gave, under conditions which lead to the flavone, 3-*bromo*-4′-*methoxy*-6-*methylflavanone*, coarse, colourless crystals, m. p. 142° (possibly not quite pure), whereas under conditions which cause the production of benzylidenecoumaranone, 4-hydroxy-*m*-tolyl α-bromo-4-methoxystyryl ketone, m. p. about 107°, was formed. 2-*Hydroxyphenyl* 4-*methoxystyryl ketone dibromide*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4{\cdot}OMe$, pale yellow, lustrous crystals, m. p. 133°, or its *acetate*, is converted by similar methods into 4′-*methoxyflavone*, $C_6H_4{<}\begin{matrix}CO-CH\\ \Vert\\ O---C{\cdot}C_6H_4{\cdot}OMe\end{matrix}$, m. p. 157—158°, or 4′-*methoxybenzylidenecoumaranone*, $C_6H_4{<}{}^{CO}_{O-}{>}C{:}CH{\cdot}C_6H_4{\cdot}OMe$, m. p. 126°. In like manner, 3′ : 4′-*methylenedioxyflavone*, pale yellow, slender needles, m. p. 200—201°, and 3′ : 4′-methylenedioxybenzylidenecoumaranone, m. p. 192°, are derived. Attempts to prepare benzylidenecoumaranones by the action of alkali on the bromides of 2-acetoxyphenyl styryl ketones or 4-hydroxy-*m*-tolyl styryl ketones yielded only flavones or substances of unknown constitution, from which the desired substances could not be isolated.

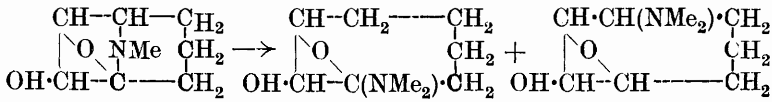
o-*Allyl*-p-*cresol dibromide*, colourless needles, m. p. 78·5—79·5°, is transformed by alcoholic sodium hydroxide solution into 2 : 5-dimethylcoumarone, b. p. 220—221°, $d_4^{11\cdot7}$ 1·0409, d_4^{20} 1·033, $n_\alpha^{11\cdot7}$ 1·55298, $n_D^{11\cdot7}$ 1·55875, $n_\beta^{11\cdot7}$ 1·57527, $n_\gamma^{11\cdot7}$ 1·59005, n_D^{20} 1·5550.

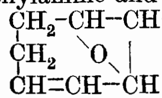
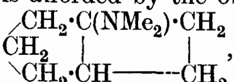
H. W.

The Action of Sodium on Phenyl Acetate. WILLIAM HENRY PERKIN, JUN. (T., 1921, **119**, 1284—1294).

The Degradation of Scopoline. K. HESS (*Zeitsch. angew. Chem.*, 1921, **34**, 393—396).—The irregularities observed previously (A., 1920, i, 81) in the Hofmann degradation of scopoline can be avoided if care is taken that silver does not pass into solution during the treatment of scopoline methiodide with silver oxide and if the fission of the quaternary base is effected in a high vacuum. A mixture of unsaturated compounds is thus obtained which, after being hydrogenated, contains four isomerides, two of which are crystalline, m. p. 53° and 78° (picrates, m. p. 183° and 153° respectively), whereas the other two are non-crystalline (picrates, m. p. 233° and 194° respectively). Since the presence of the vicinal

hydroxy-group in scopoline renders the elimination of the amino-group impossible, attempts have been made to replace it by the methoxy-group by successive treatment with thionyl chloride and sodium methoxide. In this manner, the substance, m. p. 53°, gives a *chloride*, quadratic plates, m. p. 45°, in which the chlorine atom is replaceable by the methoxy-group in the normal manner. On the other hand, the mixture of liquid isomerides yields a *chloro*-derivative from which a methoxy-compound is obtained, identical with the methyl ether isolated previously (*loc. cit.*) by the Hofmann degradation of scopoline, and directly preparable by the action of sodium methoxide on the non-chlorinated initial material. The observations are explained by the assumption that the following changes occur during degradation and reduction.



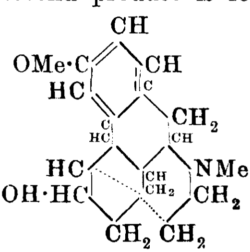
These substances behave differently on further degradation, since treatment of the crystalline product (latter formula) leads to the smooth elimination of trimethylamine and formation of a nitrogen-free unsaturated *substance*, , b. p. 70—71°/13 mm. Further confirmation of the structure ascribed to the bases is afforded by the observation that each yields the same *substance*, , b. p. 165—166°/normal pressure (*picrate*, m. p. 157—158°), when treated successively with red phosphorus and hydriodic acid and zinc and dilute sulphuric acid.

The paper concludes with an exhaustive reply to the recent criticisms of the author's formula for scopoline (Gadamer and Hammer, this vol., i, 588). H. W.

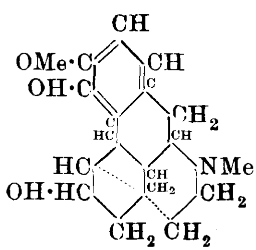
Dihydrothebaine, Dihydrothebainone, and Dihydrothebainol. A. SKITA [with F. F. NORD, J. REICHERT, and P. STUKART] (*Ber.*, 1921, **54**, [*B*], 1560—1564).—Dihydrothebaine is readily obtained by the catalytic reduction of an aqueous solution of thebaine hydrochloride in the presence of colloidal palladium; it has $[\alpha]_D^{20}$ −266·86° in benzene solution, and yields a single methiodide, needles, m. p. 257° (contrast Freund and Speyer, this vol., i, 125) and a *hydrogen citrate*, decomp. 88—90°. Thebaine hydrochloride is catalytically reduced in the presence of colloidal platinum to a mixture of tetrahydrothebaine, m. p. 143—144°, which is insoluble in alkali, and a substance which dissolves in alkali and, after purification through its *oxime*, m. p. 250°, is identified as dihydrothebainone, m. p. 137—138°, $[\alpha]_D^{20}$ −80·12°, in alcoholic solution; the latter is the sole product when reduction of thebaine is effected in acetic acid solution. The corresponding *methiodide* has m. p. 116°. The substance, m. p. 150—151°, after softening at 140° (methiodide,

m. p. 150°) described by Freund and Speyer (*loc. cit.*), is a mixture of dihydrothebainone and a more completely hydrogenated base. Dihydrothebainone is reduced by hydrogen and platinum in aqueous acid solution to dihydrothebainol, slender needles, m. p. 165°, $[\alpha]_D^{20}$ −36·5°, in alcoholic solution; the corresponding *methiodide* has m. p. 273°, whilst the *bisphenylurethane* has m. p. 175°. The reduction of thebaine in acid or neutral solution yields primarily dihydrothebaine, which, under the latter conditions, can be further reduced to tetrahydrothebaine, whilst in acid solution it gives mainly dihydrothebainone and dihydrothebainol. A specific difference between the actions of spongy platinum and colloidal palladium, as presumed by Freund and Speyer, does not exist, the observed differences being due to variation of the active surface of the catalyst. H. W.

Reduction of Dihydrothebainone. EDMUND SPEYER and SIGURD SIEBERT (*Ber.*, 1921, **54**, [*B*], 1519—1531).—The electrolytic reduction of dihydrothebainone (Freund and Speyer, this vol., i, 125) has been investigated. The main product is insoluble in alkali and from its origin, mode of formation, and properties is considered to be "dihydrothebacodine" (annexed formula I); a second product is formed in minor amount which is soluble in alkali hydroxide, and thus contains the phenolic group of the original substance intact. Its similarity to thebainol leads the authors to term it *dihydrothebainol* (formula II).



(I.)



(II.)

Reduction of dihydrothebainone is effected in sulphuric acid solution with prepared lead electrodes and high current density. The crude product is purified by treatment with sodium hydroxide solution, which dissolves dihydrothebainol, but does not affect *dihydrothebacodine*. The latter crystallises from alcohol in pale pink, prismatic rods ($+\frac{1}{2}H_2O$), m. p. 149°. It gives a *hydriodide*, needles, m. p. 151—152°, and a *methiodide*. The latter is converted by concentrated potassium hydroxide solution into *demethyldihydrothebacodine*, $C_{19}H_{27}O_2N$, needles, m. p. 147—150°, which gives a non-crystalline *methiodide*, from which, by further action of potassium hydroxide solution, trimethylamine and the *substance*, $C_{17}H_{20}O_2$, needles, m. p. 109—110°, are obtained. Dihydrothebacodine is converted by phosphorus pentachloride in the presence of chloroform into *chlorodihydrothebacodide*, which forms ill-defined rods, m. p. 132°, after softening at 125° [*methiodide*, m. p. 240—241° (decomp.)]. Reduction of the chloro-compound with sodium and alcohol leads to the formation of *deoxydihydrothebacodine*, $C_{18}H_{25}ON$, golden-yellow leaflets, m. p. 146°, after

softening at 137—138°. The corresponding *hydriodide*, decomp. 252°, after shrinking at 250°, and *methiodide*, coarse, rhombic crystals, m. p. 266—267° after softening at 264°, are described. The latter is converted by concentrated potassium hydroxide solution into *demethyldeoxydihydrothebacodine*, rods (+1EtOH), m. p. 132—133°, which is transformed successively into the *methiodide*, m. p. 261—262°, and the nitrogen-free *substance*, $C_{17}H_{29}O$, m. p. 98—99°, and trimethylamine.

Dihydrothebainol (formula II) crystallises in rods ($+\frac{1}{2}H_2O$), decomp. 142° after softening at 138° (the *hydrochloride*, decomp. 268°, and *hydriodide*, are described). The presence of a phenolic hydroxyl group is proved by the ready solubility of the substance in a solution of alkali hydroxide and by the preparation of the corresponding *methyl ether*, $C_{19}H_{27}O_3N$, small, quadratic leaflets, m. p. 186° after softening at 181° (*methiodide*, m. p. 284—285°). *Dihydrothebainol methiodide* forms long, hexagonal rods, m. p. 280°, and is transformed in the usual manner into *demethyldihydrothebainol*, which is an unstable oil (*hydriodide*, coarse, hexagonal rods, m. p. 179—180°). *Demethyldihydrothebainol methiodide*, m. p. 281—282°, is decomposed by concentrated potassium hydroxide solution into trimethylamine, and an oily *compound*, which is free from nitrogen but could not be caused to crystallise. H. W.

Partial Hydrogenation of Pyridinecarboxylic Esters. OTTO MUMM and WILHELM BETH (*Ber.*, 1921, **54**, [*B*], 1591—1603).—The reduction of pyridine derivatives to the corresponding hexahydro-compounds does not present particular difficulties, but up to the present it has not been found possible to arrest reduction at the dihydro-stage; those compounds belonging to the latter class are almost exclusively obtained by the Hantzsch synthesis and their number is restricted. The authors have now found in activated aluminium a reagent which permits the direct preparation of dihydro-derivatives; reduction by this method has been applied with normal results in a number of instances. An unusual behaviour is, however, observed with 2 : 6-dimethylpyridine-3 : 5-dicarboxylic ester, reduction of which leads to the union of two pyridine nuclei presumably through the carbon atoms in position 4, yielding a "primary" ester which is dissociable into radicles in much the same manner as are the alkylated tetrahydro-4 : 4′-dipyridyls recently described by Emmert (A., 1917, i, 221; this vol., i, 268).

Ethyl 2 : 6-dimethylpyridine-3 : 4-dicarboxylate is smoothly reduced by activated aluminium in boiling moist ethereal solution to *ethyl* 2 : 6-*dimethyldihydropyridine*-3 : 4-*dicarboxylate*,

$$\begin{array}{l} \mathrm{CMe{\cdot}CH_2{\cdot}CH{\cdot}CO_2Et} \\ \| \qquad\qquad\quad | \\ \mathrm{N{\cdot}CMe{=\!=}C{\cdot}CO_2Et} \end{array},$$

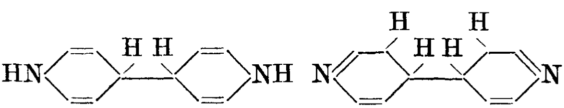
colourless, rhombic plates, m. p. 85°. It is readily dehydrogenated by chromic anhydride and acetic acid, but not by nitrous acid, with which reaction appears to follow an unusual course which has not been elucidated completely. It is very stable towards cold alkali, and does not appear to be simply decomposed in boiling

solution. It is slowly oxidised on exposure to air to a mixture of 2 : 6-dimethylcinchomeronic ester, and the *ester*,

$$N{<}\begin{matrix}CMe\cdot CH(OH)\text{-}\\ CMe{:}C(CO_2Et)\end{matrix}{>}CH\cdot CO_2Et,$$

m. p. 156° (decomp.), which slowly, when preserved at the ordinary temperature, but very rapidly when heated, loses water and gives the 2 : 6-dimethylcinchomeronic ester. The dihydro-ester is converted by distillation with soda-lime into 2 : 6-lutidine. Ethyl collidinedicarboxylate is reduced by activated aluminium to dihydrocollidinedicarboxylic ester, m. p. 130°, identical with the product obtained by Hantzsch's method. Similarly, 4-phenyllutidinedicarboxylic ester yields 4-phenyldihydrolutidinedicarboxylic ester, m. p. 156°, whereas 2-methyl-6-phenylcinchomeronic ester does not appear to be affected.

Ethyl 2 : 6-dimethylpyridine-3 : 5-dicarboxylate is reduced by aluminium in boiling alcoholic solution to the "primary" *ester*, $NH{<}\begin{matrix}CMe\cdot C(CO_2Et)\\ CMe\cdot C(CO_2Et)\end{matrix}{>}CH\cdot CH{<}\begin{matrix}C(CO_2Et)\cdot CMe\\ C(CO_2Et)\cdot CMe\end{matrix}{>}NH$, a crystalline, chrome-yellow powder, m. p. about 220° after previous softening, and after re-solidification, at 70°. The molecular weight could not be determined, since a suitable solvent could not be found. The ester is very readily oxidised by air in the presence of such traces of acid vapour as are usually found in a laboratory, but is reasonably stable when preserved over soda-lime. When distilled in a high vacuum, it yields equimolecular amounts of lutidinecarboxylic ester and dihydrolutidinedicarboxylic ester. It is converted almost quantitatively when heated at 160—170° in the absence of air into an isomeric ester, small, greenish-yellow needles melting rather indefinitely at 230°, which differs from the primary ester in its complete stability towards air. It is readily oxidised by concentrated nitric acid to lutidinedicarboxylic ester, and, when distilled in a high vacuum, gives a mixture of this substance and dihydrolutidinedicarboxylic ester. The differences between the primary (I) and transformation (II) esters are indicated in the annexed formulæ. H. W.



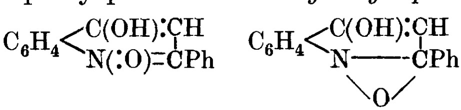
(I.) (II.)

The Doebner-Miller Quinaldine Synthesis. WILLIAM HOBSON MILLS, JOHN EDMUND GUY HARRIS, and HERBERT LAMBOURNE (T., 1921, **119**, 1294—1300).

Derivatives of certain *o*-Nitroketones. II. S. GABRIEL and WILH. GERHARD (*Ber.*, 1921, **54**, [*B*], 1613—1618).—The peculiar behaviour of *o*-nitrobenzoylacetone on reduction (this vol., i, 441) has caused the authors to examine *o*-nitrobenzoylacetophenone.

o-Nitrodibenzoylacetonitrile, $NO_2\cdot C_6H_4\cdot CO\cdot CHBz\cdot CN$, pale yellow

plates, m. p. 123·5—124°, is prepared by the action of *o*-nitrobenzoyl chloride, m. p. 23·5°, on ω-cyanoacetophenone in benzene solution in the presence of sodium powder. Attempts to eliminate the cyano-group by means of sulphuric acid were unsuccessful. The substance is reduced by hydriodic acid and red phosphorus to 4-*hydroxy*-3-*cyano*-2-*phenylquinoline*, $C_6H_4<\begin{matrix}CO\cdot CH\cdot CN\\ N{=}CPh\end{matrix}$, a colourless, crystalline substance which does not melt below 287°. *Ethyl* o-*nitrodibenzoylacetate*, $NO_2\cdot C_6H_4\cdot CO\cdot CHBz\cdot CO_2Et$, quadratic prisms, m. p. 87·5—88°, is prepared from *o*-nitrobenzoyl chloride, ethyl benzoylacetate, and sodium ethoxide, and is reduced by stannous chloride to *ethyl* 4-*hydroxy*-2-*phenylquinoline*-3-*carboxylate*, a crystalline powder, m. p. 254—255° (decomp.). Treatment with boiling aqueous sulphuric acid converts the ester into o-*nitrodibenzoylmethane*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2Bz$, needles, m. p. 116°, which is reduced by hydriodic acid or by stannous chloride to 4-hydroxy-2-phenylquinoline and 4-*hydroxy*-2-*phenylquinoline oxide* (annexed formula I or II), yellow crystals, m. p. 249·5° to a cloudy liquid (the *hydrochloride* and *nitrate* are described). When oxidised with nitric acid in acetic acid solution, the base gives 3-*nitro*-4-*hydroxy*-2-*phenylquinoline*, yellow needles, m. p. 246—247°.



(I.) (II.)

m-*Nitrobenzoylacetone*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot COMe$, obtained by boiling ethyl *m*-nitrobenzoylacetoacetate with dilute sulphuric acid, crystallises in needles, m. p. 114—115°; it is reduced by stannous chloride and concentrated hydrochloric acid to m-*aminobenzoylacetone*, pale yellow, flattened needles, m. p. 66—67°. In a similar manner, p-*nitrobenzoylacetone*, needles, m. p. 102° after softening at 98°, is converted into p-*aminobenzoylacetone*, lemon-yellow crystals, m. p. 94—95°. H. W.

2-Phenyl-5-chloromethyloxazolidine. MAX BERGMANN, FRITZ RADT, and ERWIN BRAND (*Ber.*, 1921, **54**, [*B*], 1645—1652).—It has been shown recently (Bergmann, Brand, and Dreyer, this vol., i, 444) that 2-phenyl-5-hydroxymethyloxazolidine forms an excellent starting-point for the synthesis of glycerides of known constitution, and in this connexion the preparation of 2-phenyl-5-chloromethyloxazolidine is now described. The experiments have also served a second purpose, since it has been found that the bromination of acylated allylamines frequently leads, not only to the corresponding dibromides, but also to considerable quantities of salts of halogenated esters of the type $CH_2Br\cdot CH(OAcyl)\cdot CH_2\cdot NH_2,HBr$ or $OAcyl\cdot CH_2\cdot CHBr\cdot CH_2\cdot NH_2,HBr$ (the experimental details will be published subsequently). The same esters can be prepared by the action of hot water on the normal bromides, but it is thereby uncertain whether the ester group becomes attached to the α- or β-carbon atom. Now it is found that the chlorination of allylbenzamide gives the normal dichloride and a chlorobenzoyl-

oxypropylamine hydrochloride, $CH_2Cl\cdot CH(OBz)\cdot CH_2\cdot NH_2,HCl$ or $OBz\cdot CH_2\cdot CHCl\cdot CH_2\cdot NH_2,HCl$, and that the corresponding free base is identical with the product of the hydrolysis of 2-phenyl-5-chloromethyloxazolidine, and hence has the former formula. It would therefore appear that the halogen atom attached to the intermediate carbon atom is alone concerned with the conversion of dihalogenated acid amides into ester salts.

2-*Phenyl*-5-*chloromethyloxazolidine*, $CHPh<\begin{matrix}O\text{---}CH\cdot CH_2Cl\\ NH\text{---}CH_2\end{matrix}$, long, colourless needles, m. p. 82—83°, is prepared by the action of benzaldehyde and solid potassium carbonate on a solution of γ-chloro-β-hydroxypropylamine hydrochloride. By acylation and subsequent elimination of benzaldehyde, it is converted into *benzo-γ-chloro-β-hydroxypropylamide*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot NHBz$, colourless, hexagonal plates, m. p. 107—108° (corr.), and p-*nitrobenzo-γ-chloro-β-hydroxypropylamide*, long, colourless needles, m. p. 110—112°; during the preparation of the latter, it was found possible to isolate the intermediately formed 3-p-*nitrobenzoyl*-2-*phenyl*-5-*chloromethyloxazolidine*, colourless prisms or plates, m. p. 120—122° (corr.). Phenylchloromethyloxazolidine is converted by alcoholic potassium hydroxide solution or by alcoholic sodium ethoxide solution into *phenylethoxymethyloxazolidine*, b. p. 127—129°/1·1 mm., and *benzylidene-epihydrinamine*,

$$CHPh:N\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ |\\ O\end{matrix},$$

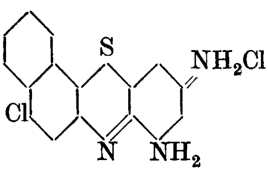
b. p. 102—104°/1·1 mm.; the latter is converted by alcoholic ammonia and subsequent loss of benzaldehyde into αγ-diamino*iso*propyl alcohol [hydrochloride, m. p. 175—177°, picrate, yellow prisms, m. p. 240—241° (decomp.), *oxalate*, leaflets, m. p. 215°].

A solution of benzoallylamide in moist, ice-cold chloroform is converted by a slow current of chlorine into *benzodichloropropylamide*, long needles, m. p. 100—101° (corr.) after softening at 99°, and *γ-chloro-β-benzoyloxypropylamine hydrochloride*, clusters of needles or six-sided prisms, m. p. 191° (corr.). The latter is transformed by the calculated quantity of aqueous potassium hydroxide into benzo-γ-chloro-β-hydroxypropylamide, m. p. 107—108°.

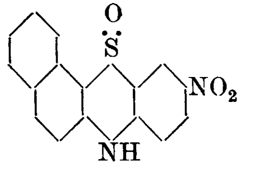
H. W.

The Synthesis of Oxazines and Thiazines of the Naphthalene Series. ZDENKA LUDWIG-SEMELIĆ (*Rev. Chim.*, 1921, **1**, 84—88, 129—136).—A continuation of a paper part of which has already appeared (see this vol., i, 448).

Other methods of preparing βα-*naphthaphenoxazine*-5-*anil*, orange-yellow crystals, m. p. 216°, are (i) fusion of 2-hydroxy-1 : 4-naphthaquinone monoanil with *o*-aminophenol hydrochloride, and (ii) oxidation of the crude product obtained by fusing 1 : 2-dihydroxynaphthalene with *o*-aminophenol hydrochloride by means of ferric chloride in the presence of aniline. It forms a *hydrochloride*, red needles with a green, metallic reflex, and a *platinichloride*, $(C_{22}H_{15}ON_2Cl)_2PtCl_4$, small, dark brown crystals.



(I.)



(II.)

5-*Chloro*-8 : 10-*diamino*-αβ-*naphthaphenothiazonium chloride* (I), dark blue needles, and 10-*nitro*-αβ-*naphthaphenothiazine S-oxide* (II), small, orange-yellow needles, are obtained from the product of nitrating αβ-naphthaphenothiazine as previously described (*loc. cit.*). C. K. I.

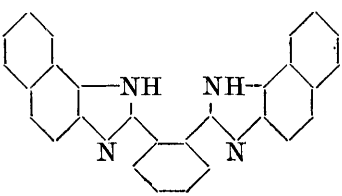
***iso*Cyanines and Carbocyanines: Their Constitution and their Activity as Photographic Sensitisers.** (SIR) WILLIAM POPE (*Bull. Soc. chim. Belg.*, 1921, **30**, 169).—A lecture delivered under the auspices of the Solvay Chemical Institute on March 19, 1921. A. A. E.

Dyes of the Pyrazolone Series. MARY JOHNSON (*J. Soc. Chem. Ind.*, 1921, **40**, 176T—178T).—Full directions are given for the preparation of tartrazine (trisodium salt of the *p*-sulphophenylhydrazone of 1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid) by the action of sodium dihydroxytartrate on phenylhydrazine-*p*-sulphonic acid. If the latter is replaced by the corresponding meta-derivative, the *trisodium* salt of the m-*sulphophenylhydrazone* of 1-m-*sulphophenyl*-5-*pyrazolone*-3-*carboxylic acid*, yellow powder ($+6H_2O$), is obtained. The *trisodium* salt of the p-*sulphonaphthylhydrazone* of 1-p-*sulphonaphthyl*-5-*pyrazolone*-3-*carboxylic acid*, dark scarlet powder ($+6H_2O$), is prepared in an analogous manner. 1 : 5-Naphthylhydrazinesulphonic acid (the preparation of which from α-aminonaphthalene-5-sulphonic acid is described in detail) yields the *trisodium* salt of the 5-*sulphonaphthylhydrazone* of 1-(5-*sulphonaphthyl*)-5-*pyrazolone*-3-*carboxylic acid*, dark red powder ($+14H_2O$). The absorption spectra of these substances are all of the same general type characterised by a broad band originating in the green. The original tartrazine, however, shows the greatest absorption, and the use of the newer dyes for photographic screen work offers no advantage. They all act as dyes towards wool and silk. H. W.

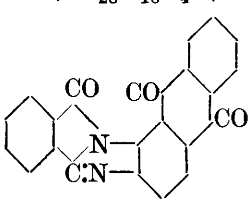
Dyes Derived from Phenanthraquinone. EDWIN ROY WATSON and SIKHIBHUSHAN DUTT (T., 1921, **119**, 1211—1221).

Condensations of Aromatic Diamines with Phthalic Anhydride. II. HANS LIEB and GUSTAV SCHWARZER (*Monatsh.*, 1920, **41**, 573—582; cf. A., 1919, i, 174).—When heated together in a sealed tube at 250°, phthalic anhydride (1 mol.) and 1 : 2-naphthylenediamine (2 mols.) yield *o*-phenylenedi-1 : 2-naphthiminazole. Phthalic anhydride and 1 : 2-diaminoanthraquinone give benzoyleneanthraquinoniminazole when heated together in any proportions and in either an open or closed vessel; by sodium

or ammonium hydroxide this compound is converted into the intense red salt of phenylanthraquinoniminazole-*o*-carboxylic acid, but the acid itself cannot be isolated, as it immediately loses water and forms the lactam again. Fusion together of 1 : 5-diaminoanthraquinone and phthalic anhydride yields various condensation products: 1 mol. of the diamine with at least 2 mols. of the anhydride yield diphthaloyl-1 : 5-diaminoanthraquinone (anthraquinone-1 : 5-diphthalimide) almost quantitatively, whereas 1 mol. of each give phthaloyl-1 : 5-diaminoanthraquinone and also the diphthaloyl derivative, and, when heated in a sealed tube, also a dark red compound, which is soluble in concentrated sulphuric acid and is reprecipitated on addition of water. The preparation of condensation products of *p*- and *m*-phenylenediamine with phthalic anhydride (cf. Biedermann, A., 1877, ii, 783; Meyer, A., 1903, i, 442) has been simplified and the action on them of zinc dust and acetic acid investigated.



o-*Phenylenedi*-1 : 2-*naphthiminazole*, $C_{28}H_{18}N_4$ (annexed formula), crystallises in yellow rods, softening at 302°, m. p. 304°. Its *acetyl* derivative, $C_{32}H_{22}O_2N_4$, colourless, rhombic plates, m. p. 236° (decomp.), and *benzoyl* derivative, $C_{42}H_{26}O_2N_4$, almost colourless plates, m. p. 237—238°, were prepared.



Benzoyleneanthraquinoniminazole, $C_{22}H_{10}O_3N_2$ (annexed formula), crystallises in yellow needles, m. p. 354° (decomp.).

Diphthaloyl-1 : 5-*diaminoanthraquinone*,

$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot C_6H_3{<}\substack{CO\\CO}{>}C_6H_3\cdot N{<}\substack{CO\\CO}{>}C_6H_4,$$

forms crystals, m. p. 435—436° (decomp.).

Phthaloyl-1 : 5-*diaminoanthraquinone*,

$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot C_6H_3{<}\substack{CO\\CO}{>}C_6H_3\cdot NH_2,$$

forms crystals, m. p. 331°.

p-Aminophthalanil (monophthaloyl-*p*-phenylenediamine) has m. p. 246°, the value usually given being 250°; p-*acetylaminophthalanil*, $C_{16}H_{12}O_3N_2$, forms colourless crystals, m. p. 287—288°.

Reduction of diphthaloyl-*p*-phenylenediamine by means of zinc dust and acetic acid yields a substance, $C_{22}H_{14}O_4N_2$(?), m. p. 318—319°, which is apparently not an individual compound.

Similar reduction of diphthaloyl-*m*-phenylenediamine gave no definite results. T. H. P.

The Acidity of the Hydrogen Atoms in Uric Acid. Heinrich Biltz and Lisbeth Herrmann (*Ber.*, 1921, **54**, [*B*], 1676—1694).—All four hydrogen atoms of uric acid are acidic and can be replaced by metals, as is shown by the formation of salts from each

of the four trimethyluric acids. Generally, however, uric acid functions as a dibasic acid at most, and the precise location of the replaceable hydrogen atoms has not been elucidated. This can be effected by measurement of the dissociation constants of the four trimethyluric acids, but since it has not been established that the presence of a methyl group does not alter the acidity of the remaining hydrogen atoms, the present investigation has been extended in scope to all the methyluric acids. Measurements are effected by Sörensen's colorimetric method (A., 1909, i, 861). The results show that hydrogen atom 3 is the most acidic, and that the hydrogen salts result from its displacement by metal. Next in order is hydrogen atom 9, and the normal salts result from the displacement of these two atoms. Hydrogen atoms 1 and 7 are much weaker; their acidity is approximately equal, atom 7 being probably the weaker. The capacity of ionisation of the uric acids is not greatly influenced by the presence of methyl groups.

The investigation throws considerable light on the course of the methylation of uric acid. During the direct action of alkyl haloid on solid metallic urates it is shown that the most acidic hydrogen atom available is replaced during salt formation and the place of the metallic atom is taken by the methyl group during methylation. It should be noted that, in the salt, the metal is attached to oxygen, whereas the alkyl group is attached to nitrogen, the whole phenomenon thus resembling that observed in the alkylation of ethyl sodioacetoacetate and similar substances. The sole exception to this rule is furnished by the silver salts of 1 : 3 : 7-trimethyluric acid, which yield initially 8-alkyloxy-1 : 3 : 7-trimethylxanthines, which are subsequently converted into tetra-alkyluric acids. Methylation with methyl sulphate in alkaline solution proceeds quite differently; the methyl group does not replace the most acidic hydrogen atom, but one which has only a slight tendency towards ionisation. This is attributed to a primary addition of the components of the methyl sulphate to the nitrogen atom and subsequent elimination of methyl hydrogen sulphate. The action of formaldehyde, leading to the introduction of the hydroxymethyl group, appears to take place similarly, and this is true to a less extent of the alkylation of the methyluric acids by methyl iodide in alkaline solution. The alkylation of uric acid itself under the latter conditions proceeds in a different and complicated manner, for which an explanation is not advanced.

H. W.

Action of Chloroform on Phenylhydrazine. W. LEIGH BARNETT (*J. Soc. Chem. Ind.*, 1921, **40**, 167T—168T).—Analytical evidence is adduced to show that the primary product of the interaction of chloroform and phenylhydrazine at the ordinary temperature (this vol., i, 308; cf. Brunner and Leins, A., 1898, i, 158), m. p. 221° (decomp.), is an additive product, which is regarded as *triphenylhydrazinomethane trihydrochloride*, $CH(NH\cdot NHPh)_3,3HCl$. It reacts with moisture to form phenylhydrazine hydrochloride and formic acid.

J. K.

The Stability of Tryptophan in Baryta Hydrolysis. HERBERT ONSLOW (*Biochem. J.*, 1921, **15**, 383—392).—When caseinogen is hydrolysed by barium hydroxide solution tryptophan is not destroyed; this protection is due to the presence of other products of hydrolysis, since the destruction of tryptophan can be prevented to a great extent by the addition of crystalline amino-acids. When gelatin or zein is hydrolysed by barium hydroxide there are only traces of nitrogen to be found in the mercuric sulphate fraction, but after the addition of pure tryptophan to gelatin the total nitrogen in this fraction is equivalent to the added tryptophan. Tryptophan is more resistant to acid hydrolysis in pure condition than when present in combination in caseinogen. The precipitation of free tyrosine by the mercury reagent can be prevented by raising the concentration of the sulphuric acid from 5% to 7% by volume. Histidine is fairly stable when boiled with barium hydroxide solution and its precipitation in acid solution by mercuric sulphate is helped by the presence of other amino-acids. The total nitrogen of the mercuric sulphate fraction reaches a maximum after the casein has been hydrolysed under specified conditions for sixty to seventy hours. S. S. Z.

The Nature of the Substances Precipitated by Mercuric Sulphate from Hydrolysed Caseinogen, with Reference to the Estimation and Isolation of Tryptophan. HERBERT ONSLOW (*Biochem. J.*, 1921, **15**, 392—399).—The character of the mercuric sulphate fraction in the hydrolysis of casinogen under different conditions has been studied. This fraction was found to contain a number of amino-acids which are probably in combination with tryptophan. Tyrosine does not separate early in pancreatic digestion of the caseinogen. Good yields of tryptophan are obtained from caseinogen if the decomposed mercuric sulphate precipitate is redigested and extracted with butyl alcohol. S. S. Z.

Tanning (Hardening) of Gelatin by Formaldehyde. W. MOELLER (*Kolloid Zeitsch.*, 1921, **29**, 45—55).—The action of formaldehyde solutions on gelatin solutions of varying composition has been investigated. It is shown that the hardening of gelatin in these circumstances is a two-phase process. The actual hardening of the portion of the gelatin which may be hardened is a physical process in which only the coagulable portion of the gelatin takes part. The non-coagulable portion of the gelatin enters into a chemical reaction with the formaldehyde, with the formation of methylene amino-acids. The portion of the gelatin capable of hardening corresponds with the coagulation value of the untreated gelatin. If the coagulable part of the gelatin is reduced by hydrolysis in consequence of the action of hydrogen ions, then the portion capable of hardening is also reduced. The constituents of the formaldehyde solution which are capable of hardening are the insoluble colloidal polymerides of formaldehyde, which are only formed during the action on the gelatin. J. F. S.

Donnan Equilibrium and the Physical Properties of Proteins. III. Viscosity. JACQUES LOEB (*J. gen. Physiol.*, 1921,

3, 827—842; cf. this vol., i, 627).—The high viscosity of freshly prepared gelatin solutions is influenced by the hydrogen-ion concentration. Solutions of egg-albumin prepared under similar conditions show a comparatively low viscosity and are practically unaffected by the H-ion concentration. Suspensions of powdered gelatin in water manifest a slightly higher viscosity than gelatin solutions of similar concentration; in this case also the viscosity is influenced by the H-ion concentration. The volume occupied by the suspended gelatin varies as the viscosity, which is in agreement with the theories of viscosity. The influence of the H-ion concentration on the volume occupied by the gelatin granules in suspension is due to the existence of a Donnan equilibrium between the granules and the surrounding solutions. S. S. Z.

Organic Compounds of Arsenic. IV. Action of Alkyl Haloids on Cacodyls and a New Mode of Formation of Tetra-alkyl-(aryl)-arsonium Tri-iodides. WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, **54**, [*B*], 1437—1465).—The action of methyl iodide on cacodyl has been shown by Cahours and Riche to lead to the formation of tetramethylarsonium iodide and iododimethylarsine. Since, however, they operated under somewhat drastic conditions, it appeared not unlikely that the hitherto unknown hexamethyldiarsonium di-iodide was formed intermediately. To investigate this point, the authors have therefore subjected cacodyl, tetraphenyldiarsine, and *s*-diphenyldimethyldiarsine to the gentle action of alkyl haloids, but their results only serve to confirm those of Cahours and Riche. The results are most readily explained on the hypothesis that the primary product of the reaction is of the type $AsR_2I{\cdot}AsR_2Me$, which decomposes, before further addition of alkyl haloid can occur, in accordance with the scheme:

$$AsR_2I{\cdot}AsR_2Me \longrightarrow AsR_2I + AsR_2Me \xrightarrow{CH_3I} AsMe_2R_2I.$$

The probable truth of this explanation is supported by a large number of instances drawn from the literature on compounds of arsenic.

Secondary iodoarsines are smoothly and often almost quantitatively converted by methyl iodide at 100° into the quaternary arsonium tri-iodides, and since the latter are readily obtained from chloroarsines and sodium iodide in acetone solution, whereas the quaternary compounds are easily transformed into tertiary arsines, the reaction promises to be of considerable importance in the preparation of the latter. The action of methyl iodide on secondary chloro-, bromo-, cyano-, and thiocyano-arsines, investigated in the hope of isolating substances of the type AsR_4ClI_2, etc., leads unexpectedly in all those cases in which a per-haloid is produced, to the formation of the tri-iodide. The course of the reaction between methyl iodide and a secondary arsine is represented by the scheme: $AsR_2I \xrightarrow{MeI} AsR_2MeI_2 \xrightarrow{MeI} AsR_2Me_2I_3$; the tri-iodide, however, is invariably accompanied by the arsonium iodide as a result of the action of the tri-iodide on unchanged initial material, for example, $AsMe_2Br + AsMe_4I_3 \longrightarrow AsMe_2BrI_2 + AsMe_4I$.

The following individual substances are described: Phenyldimethylarsine (from magnesium methyl bromide and phenyldichloroarsine), b. p. 193—200°; *phenyltrimethylarsonium bromide*, compact crystals, m. p. 284° (decomp.) (corresponding *platinichloride*, brown leaflets, m. p. 197—200°; *picrate*, orange-yellow needles, m. p. 145°); s-*phenylmethylarsine oxide*, $(AsPhMe)_2O$, an almost colourless, highly refractive liquid, b. p. about 94°/11 mm.; s-*diphenyldimethyldiarsine* (from the oxide and crystalline phosphorous acid), m. p. about 70°; tetraphenyldiarsine [phenylcacodyl], the isolation of which in the dry condition is described and the necessary apparatus depicted.

Cacodyl and methyl bromide at 100° give tetramethylarsonium bromide and trimethylarsine dibromide. Methyl iodide (2 mols.) and cacodyl (1 mol.) at the ordinary temperature yield tetramethylarsonium iodide, but with excess of the alkyl haloid (5 mols.) an equimolecular mixture of tetramethylarsonium iodide and tri-iodide is produced, which can be separated by taking advantage of the solubility of the latter and insolubility of the former in acetone. In a similar manner, phenyltrimethylarsonium bromide, m. p. 283°, and phenylmethylbromoarsine are formed from *s*-diphenyldimethyldiarsine and methyl bromide, whereas phenyltrimethylarsonium iodide, m. p. 244°, is obtained when methyl iodide is used. Diphenyldimethylarsonium iodide, m. p. 190°, and diphenyliodoarsine, m. p. 40·5°, are similarly derived from tetraphenyldiarsine. Arsenobenzene and methyl iodide at 100° give phenyltrimethylarsonium iodide, m. p. 248°, and the corresponding tri-iodide, m. p. 103°; the relative amount of the latter renders impossible Bertheim's explanation of its production as due to iodine liberated by the sealing of the tube (cf. A., 1914, i, 344), and its formation must be attributed to the reactions: $AsPh{:}AsPh \xrightarrow{MeI} AsPhI{\cdot}AsPhMe \xrightarrow{MeI} AsPhMeI{\cdot}AsPhMeI \longrightarrow 2AsPhMeI \xrightarrow{4MeI} 2AsPhMe_3I{:}I_2$. [Arsenobenzene and trimethylphenylarsonium tri-iodide give phenyldiiodoarsine and trimethylphenylarsonium iodide.]

Cacodyl bromide, b. p. 128—129°, is most conveniently prepared by the reduction of cacodylic acid with sodium hypophosphite in the presence of concentrated hydrobromic acid at a temperature below 60°; it is converted by methyl iodide into tetramethylarsonium tri-iodide and by methyl bromide into trimethylarsine dibromide. Cacodyl iodide, prepared by the action of the chloride on a solution of sodium iodide in acetone, has m. p. 154—155°, in agreement with the observation of Burrows and Turner (T., 1920, **117**, 1373). Cacodyl cyanide, m. p. 32·5°, is most conveniently prepared by the action of an excess of anhydrous hydrocyanic acid on cacodyl oxide at 100°. Phenylmethylchloroarsine and methyl iodide yield phenyltrimethylarsonium tri-iodide, m. p. 103°; the same compound is also obtained from phenylmethyliodoarsine, a golden-yellow liquid, b. p. 143—144°/17—18 mm. (cf. Burrows and Turner, *loc. cit.*). Diphenyldimethylarsonium tri-iodide, violet needles, m. p. 69·5°, is obtained from diphenylchloroarsine and (together with diphenyliodoarsine, m. p. 40·5°) from diphenylbromoarsine; the latter has been isolated as almost colourless

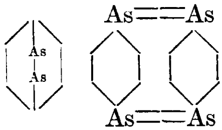
leaflets, m. p. 54°. Diphenyliodoarsine forms yellow, hexagonal crystals, m. p. 40·5°; like the corresponding cyanide and thiocyanate, it is converted by methyl iodide into diphenyldimethylarsonium tri-iodide, m. p. 69°. *Triphenylarsine di-iodide*, a yellow powder, m. p. 130—140° (from triphenylarsine and iodine in light petroleum solution) is transformed by methyl iodide into *triphenylmethylarsonium tri-iodide*, lustrous, brown leaflets, m. p. 107°. Cacodyl bromide and tetramethylarsonium tri-iodide yield tetramethylarsonium iodide, m. p. 325°, in addition to other products which were not completely investigated. Phenyltrimethylarsonium bromide is completely converted into the corresponding iodide and methyl bromide by an excess of methyl iodide.

Ethyldi-iodoarsine, b. p. 122·7°/11 mm., is conveniently prepared by the interaction of the dichloro-compound and sodium iodide in the presence of dry acetone; it gives crystalline compounds with pyridine and quinoline. It is not attacked by ethyl iodide at 100°. Similarly, methyl iodide is without action on phenyldi-iodoarsine, m. p. 15°, b. p. 185°/10 mm. (cf. Burrows and Turner, *loc. cit.*). *s*-Diphenyldi-iododiarsine and methyl iodide give phenyltrimethylarsonium tri-iodide and phenyldi-iodoarsine; the relatively small quantity of the former which is produced is shown to be due to the action of the tri-iodide first formed on diphenyldi-iodoarsine, which results in the production of phenyltrimethylarsonium iodide and phenyldi-iodoarsine.

It is shown that, in certain circumstances, the reaction with methyl iodide can be used for the detection of the presence of the individual components of mixtures such as phenyldi-iodoarsine, phenylmethyliodoarsine, and phenyldimethylarsine.

Diphenyldimethylarsonium tri-iodide is transformed by an alcoholic solution of iodine into the *compound* $AsMe_2Ph_2I,I_8$, m. p. 56°, which loses iodine readily. H. W.

Aromatic Diarsinic Acids, and their Reduction Products. I. HANS LIEB (*Ber.*, 1921, **54**, [*B*], 1511—1519).—The preparation of phenylenediarsinic acids by the diazotisation of aminophenylarsinic acids and coupling of the diazo-solution with arsenite solution under definite conditions is described. The new acids are reduced by phosphorous acid at 200° to yellow, amorphous substances which are rich in arsenic and probably free from oxygen; they are insoluble in all media, so that it has not been found possible up to the present to distinguish between the possible formulæ (annexed).



(I.) (II.)

p-Arsanilic acid is diazotised in dilute sulphuric acid solution and, after addition of so much sodium hydroxide solution that the mixture just remains faintly acid, the diazonium compound is treated with alkaline sodium arsenite; a vigorous evolution of nitrogen occurs immediately, which is completed by warming the mixture at 50—60°; the concentrated solution deposits p-*phenylenediarsinic acid*, colourless leaflets, the yield, however, being only

moderate. The *sodium* salt, needles ($+14H_2O$), is described. When *m*-aminophenylarsinic acid is treated similarly and the conditions are so adjusted that the solution remains faintly acid after coupling, nitrogen is only very slowly evolved, and the main product is *azobenzene*-3 : 3′-*diarsinic acid*, $N_2(C_6H_4 \cdot AsO_3H_2)_2$, long, dark orange-yellow needles which evolve gas at 240° and become dark when heated further. The *tri-* or *tetra-sodium* salt, orange-yellow needles (? $+11H_2O$), is also described. If, however, coupling occurs in alkaline solution, nitrogen is vigorously evolved and m-*phenylenediarsinic acid*, colourless leaflets which decompose without melting when heated, is obtained. The *sodium* salt, $C_6H_5O_6As_2Na_3,10H_2O$, crystallises in colourless needles. The diarsinic acids are reduced by phosphorous acid at an elevated temperature to yellow, amorphous *substances* which have no distinct melting points. They are readily reconverted by dilute nitric acid, concentrated sulphuric acid, and hydrogen peroxide into the diarsinic acids. Analysis points to the presence of oxygen in them, but this is regarded as being caused partly by the difficulty of effecting their purification and partly by atmospheric oxidation.

H. W.

Mercuration of Aromatic Compounds. O. DIMROTH (*Ber.*, 1921, **54**, [*B*], 1504—1510).—The mercuration of phenolic ethers has been studied by Dimroth (A., 1902, i, 656, 849), who considered the products to be substitution compounds in which the mercury atom is united to the benzene ring. More recently, Manchot has classed them as additive compounds, for example, $[OMe \cdot C_6H_5,Hg \cdot OH]OH$ (A., 1920, i, 780). The author has now repeated Manchot's experiments. He is drawn to the conclusion that the latter's substances are neither additive compounds nor intermediate compounds of nuclear mercurated derivatives, but consist of non-homogeneous mixtures of nuclear mercurated derivatives. Manchot's error is caused by a too profound reliance on analytical results.

Contrary to Manchot's statement, the very slight alkalinity of the solution formed when his anisylmercuri-compound is treated with sodium chloride is due to the slight alkalinity of the sodium acetate formed. The constitution of Manchot's compound is most clearly shown by the observation that it is converted by iodine–potassium iodide solution into a mixture of *p*-iodoanisole and 2 : 4-di-iodoanisole. It therefore consists of *p*-anisylmercuriacetate and 2 : 4-*anisylenedimercuridiacetate*, which can actually be separated from one another by taking advantage of the more sparing solubility of the latter in benzene; it crystallises in aggregates of slender, colourless needles, m. p. 197°, after softening at 195°. In a similar manner, Manchot's product of the mercuration of phenetole could be separated into *p*-phenetylmercuriacetate (ultimately identified as *p*-phenetylmercuribromide) and *phenetylenedimercuridiacetate*, $OEt \cdot C_6H_3(Hg \cdot OAc)_2$, m. p. 183—184°. Manchot's preparation from *p*-tolyl methyl ether is a nearly pure monomercuri-substitution product containing a small amount of

material richer in mercury; the pure derivative has m. p. 136°, whereas Manchot and Bössenicker give 130—131° and 132—133° for different preparations. H. W.

Organo-derivatives of Thallium. II. Interaction of Thalliumdialkyl Hydroxides with Nitrophenols and Nitrocresols. Archibald Edwin Goddard (T., 1921, **119**, 1310—1315).

Physiological Chemistry.

Distribution of Phosphoric Acid in the Blood of Normal Infants. G. M. McKellips, I. M. De Young, and W. R. Bloor (*J. Biol. Chem.*, 1921, **47**, 53—58).—The distribution of phosphoric acid in the blood of infants less than two weeks old was determined in the manner previously described (Bloor, A., 1918, i, 557, and A., 1918, ii, 452) and the results are presented in the form of a table. Sex and weight changes appear to have little influence on the values obtained. Comparison with the values obtained for adults' blood shows little difference in the values for the corpuscles, but the organic phosphorus is higher and the lipoid phosphorus lower in the plasma of the infant than in that of the adult. E. S.

The Absorption of Calcium Salts in Man. Edward H. Mason (*J. Biol. Chem.*, 1921, **47**, 3—4).—The calcium content of blood is but little affected by the oral administration of a single large dose of calcium lactate. Calcium chloride appears to be absorbed better; its rate of absorption is not affected by its solution in dilute hydrochloric acid. E. S.

The Nature of the Reducing Substance in Human Blood. Evelyn Ashley Cooper and Hilda Walker (*Biochem. J.*, 1921, **15**, 415—422).—The reducing substance in blood is neither uric acid nor creatinine. It is destroyed by boiling with ammonia, and is insoluble in ether. Hydrochloric acid even in low concentration has also a destructive effect on it. Phenylglucosazone has been isolated from human blood. The authors have confirmed Pavy and Cammidge's observation that the reducing power of blood increases after hydrolysis with hydrochloric acid. S. S. Z.

The Salicylates. XIII. The Liberation of Free Salicylic Acid from Salicylate in the Circulation. P. J. Hanzlik (*J. Pharm. Expt. Ther.*, 1921, **17**, 385—393).—Salicylic acid is liberated from sodium salicylate at P_H 6·5—6·7, but 25% of serum prevents the liberation at P_H 5·9, so that it is improbable that free salicylic acid occurs in the circulation during life. G. B.

Basal Metabolism of Normal Women. KATHARINE BLUNT and MARIE DYE (*J. Biol. Chem.*, 1921, **47**, 69—87).—The metabolism of women, which varies irregularly at all times, shows no definite change during menstruation. There is no relation between minimum pulse rate and metabolism, nor is there a definite change in pulse rate during menstruation. E. S.

Probable Intervention of Zinc in the Phenomena of Fecundation in Vertebrate Animals. GABRIEL BERTRAND and R. VLADESCO (*Compt. rend.*, 1921, **173**, 176—179. Cf. A., 1920, i, 909; this vol., i, 282).—Further analyses of the genital organs of different animals in different stages of activity indicate that zinc plays an important part in the organism of vertebrate animals and intervenes in the process of reproduction. W. G.

The Localisation of Glycogen in the Liver and the Muscles of Dogs Fed with a View to the Maximum Production of this Reserve. (MME) Z. GRUZEWSKA and FAURÉ-FRÉMIET (*Compt. rend.*, 1921, **173**, 254—257).—A young dog, submitted to an appropriate diet, distends in some way all the cells of the hepatic lobule and accumulates therein glycogen, the result being a very large increase in the liver and the glycogen and a diminution in the protein content of the liver. The variations are individual and depend on the functional power of the organs. In an old animal the cells in the middle of the lobule are capable of storing large quantities of glycogen, whilst the small cells are surcharged with protein. The amount of glycogen found in the muscle and the heart did not show any relationship to the increase of glycogen in the liver. W. G.

Anti-thrombin: a Secretion of Nuclear Origin. The Anti-coagulating Properties of Nucleic Acids. M. DOYON (*Arch. inter. Physiol.*, 1921, **16**, 343—362; from *Physiol. Abstr.*, 1921, **6**, 310).—The author obtains from the liver, and, to a less extent, from other organs, a nucleoprotein containing 3% of phosphorus, which is precipitated by acids and alcohol and gives a weak biuret reaction. This substance, which has anti-coagulating properties, is named *anti-thrombin*, and is regarded as responsible for the non-coagulability of the blood after injections of peptone.

Nucleic acids, prepared by Neumann's method, act as anti-coagulants equally in vitro and in vivo; the anti-coagulating power resides in the phosphorus-containing part of the molecule. C. R. H.

Resistance of the Vinegar Eel to Various Agents. NAPOLEONE PASSERINI (*Staz. Sper. agr. Italiane*, 1921, **54**, 15—64).—The author has investigated the action of a number both of chemical compounds and of physical conditions on the vinegar eel, which shows pronounced resistivity towards even energetic reagents. T. H. P.

Chrysalis Oil. SÔJIRO KAWASE, KEIJI SUDA, and AKIRA FUKUZAWA (*J. Chem. Soc. Japan*, 1921, **42**, 181—235).—The constituents and the physical and chemical properties of four kinds

of chrysalis oil, and of an oil from the silkworm, have been investigated. The mixed fatty acids of the oil contain about 25% solid and 75% liquid acids. The solid acid consists of a small quantity of palmitic acid, m. p. 62—64°, methyl ester, m. p. 29—30°, with a large quantity of a new isomeric acid, iso*palmitic acid*, crystallising in flat prisms from alcohol, m. p. 57—59°. The *iso*-acid and its magnesium salt are less soluble in alcohol than palmitic acid; *methyl* iso*palmitate* has m. p. 38°. By the oxidation of the liquid acid with potassium permanganate, dihydroxystearic, sativic, linusic, *iso*linusic, and azelaic acids were isolated; whilst by the bromination, hexabromo- and dibromo-stearic acids and a small quantity of tetrabromostearic acid were produced; therefore the acid is composed of oleic, linolenic, *iso*linolenic, and linolic acids. On bromination, linolenic and *iso*linolenic acids gave two different hexabromo-derivatives, one of which is a crystalline powder, m. p. 177—180°, sparingly soluble in ether and light petroleum, and the other an oily compound, soluble in the former only. By hydrogenation of the chrysalis oil, using nickel as catalyst, the only solid acid produced is stearic acid. There is therefore no other acid than that containing eighteen carbon atoms in the liquid acid. [See further, *J. Soc. Chem. Ind.*, 1921, September.] K. K.

The Influence of Free Fatty Acids in the Intestinal Contents on the Excretion of Calcium and Phosphorus. STEPHEN VEITCH TELFER (*Biochem J.*, 1921, **15**, 347—355).—In complete exclusion of bile from the gut, fatty derivatives may form 70% of the dried fæces. This non-absorption of the fatty acids affects the normal excretion of calcium and phosphorus. The calcium is found in excess in the fæces as soaps, and the phosphorus, instead of being excreted as the tricalcium salt by the bowel, is liberated from combination with calcium and is eliminated by the urine. The degree of this deviation from the normal course of excretion is controlled by the concentration of the free fatty acids in the intestine. S. S. Z.

Creatinuria. II. Arginine and Cystine as Precursors of Creatine. E. G. GROSS and H. STEENBOCK (*J. Biol. Chem.*, 1921, **47**, 33—43; cf. A., 1919, i, 107).—The oral administration of arginine to pigs augments creatinuria, but the amount of creatine excreted is less than for an equivalent amount of casein. Cystine, normally, also causes creatinuria; in this case, however, no creatine is excreted if the reaction of the urine is made alkaline by the administration of sodium acetate, although casein and arginine remain effective under these conditions. From the results the author contends that arginine is the precursor of creatine. The production of creatinuria by cystine is possibly due to the sulphuric acid produced by its oxidation stimulating katabolism. E. S.

Creatinuria. III. The Effect of Thyroid Feeding on Creatinuria. E. G. GROSS and H. STEENBOCK (*J. Biol. Chem.*, 1921, **47**, 45—52).—The excretion of creatine by pigs on a nitrogen-free diet is augmented by the addition of sheep's thyroid to their

diet. The further addition of casein, making creatine precursors from exogenous sources available, accentuates this effect. Various hypotheses are advanced in explanation. E. S.

Transformations of Salicylic Acid in the Animal Organism. F. ANGELICO (*Arch. Farm. sperim. Sci. aff.*, 1921, **31**, 8—12).—The author finds that when sodium salicylate is administered to dogs with their food, gentisic acid appears in the urine (cf. Baldoni, A., 1908, ii, 1060; 1914, i, 1158). The uraminsalicylic acid described by Baldoni is probably impure gentisic acid. T. H. P.

Toxicity of some Thioureas and Thiuramdisulphides. P. J. HANZLIK and A. IRVINE (*J. Pharm. Expt. Ther.*, 1921, **17**, 349—355).—The minimal fatal doses per kilo. of body-weight, when given to rabbits by the stomach, are, for diphenylthiocarbamide 1·5 grams, for di-*o*-tolylthiocarbamide 3 grams, for tetraethylthiuramdisulphide, $S_2(CS{\cdot}NEt_2)_2$, 3 grams, for tetramethylthiuramdisulphide 0·35 gram. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Colloidal Condition of the Proteins in Yeast Extract. II. Yeast Phosphorus Proteins in the Sol Condition as Colloid Ferments. A. FODOR (*Kolloid Zeitsch.*, 1921, **29**, 28—45; cf. this vol., i, 81).—Three phosphorus-containing proteins, λ_1, λ_2, and λ_3, are obtained from yeast by digesting it at 37° for two hours with three times its weight of water and filtering. The brownish-yellow to golden-yellow filtrate is diluted to five times its volume with water and fractionally precipitated with *N*-hydrochloric acid. Three fractions are filtered off and constitute the λ_1, λ_2, and λ_3 proteins respectively. The filtrate contains only albumins and no phosphorus-containing protein. The three fractions after washing and grinding give rise to sols or suspensions with water, the degree of dispersion of which is greater the smaller the amount of acid used to precipitate them. The sols, regarded macroscopically, of 1% content are strongly opalescent, transparent liquids which lose their opalescence on the addition of a single drop of alkali hydroxide, whilst the addition of acid to the alkaline solution precipitates the colloid, which in the presence of sodium chloride is no longer capable of forming a sol. Addition of acid to the sol itself brings about incomplete precipitation, whilst heat has a strongly coagulating effect. The precipitation of the three proteins by acid is brought about by the following H-ion concentration: λ_1, $P_H=4\cdot92$; λ_2, $P_H=4\cdot50$, and λ_3, $P_H=4\cdot18$. Of these λ_2 occurs to the greatest extent. The ultramicroscopic properties of the three sols are described. The activity of the three sols toward a 4%

solution of glycyl-*l*-leucine at 35° has been examined. After 260 minutes' treatment the increase in the amino-nitrogen corresponds with the following quantities of *N*/50-sodium hydroxide: λ_1 1·60 c.c., λ_2 1·38 c.c., and λ_3 0·08 c.c. The addition of 3 c.c. of *N*/15-monohydrogen sodium phosphate to the reaction mixture gives an increase in amino-nitrogen in eighteen hours, equivalent to the following quantities of *N*/50-sodium hydroxide: λ_1 3·26 c.c., λ_2 4·60 c.c., and λ_3 1·51 c.c. The activity decreases parallel with the degree of dispersion. It is shown that the proteins have a considerable acid reaction and that their particles travel toward the anode; with increase in the dispersion, this cataphoresis undergoes an increase, which persists, however, only until slightly hydrated albumin ions appear. These no longer undergo cataphoresis, but constitute current conductors. J. F. S.

The Differential Dialysis of the Antineuritic and the Antiscorbutic Factors. SYLVESTER SOLOMON ZILVA and MASATARO MIURA (*Biochem. J.*, 1921, **15**, 422—427).—The antineuritic factor in autolysed yeast juice and the antiscorbutic factor in decitrated lemon juice diffuse through a collodion membrane of such permeability as permits the passage of substances such as methylene-blue, neutral red, and safranine. It is suggested that the active molecules, whether simple or associated, may be of a semi-colloid nature. S. S. Z.

The Synthesis of Vitamin-*B* by Yeasts. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1921, **15**, 438—440).—The yeasts *Saccharomyces cerevisiæ* and *S. ellipsoideus*, when grown on a synthetic medium free from vitamin-*A*, are capable of curing polyneuritis in pigeons. S. S. Z.

Utilisation of Nitrogen and of Phosphorus in the Mycelium of *Aspergillus niger*. W. VORBRODT (*Bull. acad. polonaise sci. lett., classe sci. math. et nat.*, *B*, 1919, 71—109).—In cultures of *Aspergillus* containing ammonium nitrate as the source of nitrogen, loss and not fixation of that element occurred; the ammoniacal nitrogen was used in preference to the nitrate nitrogen, although a portion of the latter was also utilised. The percentage of total nitrogen and of the different groups of nitrogenous compounds present in the mycelium depended essentially on the amount of nitrogenous nutrients present in the medium. Spores were produced more rapidly in cultures poor in ammonium nitrate than in cultures containing that salt in greater concentration; phosphoric acid exerted a similar influence on the formation of spores. Organic nitrogenous compounds were not secreted into the nutrient solution during the normal development of the mould; these compounds, especially ammonia, appeared in that solution as products of the decomposition of the mycelium as a result of the degeneration of the mould. The amount of nitrogen present as insoluble protein in the mycelium, which grew in a solution rich in both nitrogen and phosphoric acid, showed merely insignificant variations during the growth; therefore, the mould attempted to

accumulate a considerable store of these proteins as rapidly as possible. The soluble protein represented an intermediate stage of metabolism in the mycelium; the percentage of these proteins present in the mycelium varied considerably according to the composition of the medium. The proportion of ammonia present in the mycelium during its normal development was extremely small. The proportion of nitrogenous compounds not precipitated by phosphotungstic acid, and particularly of amino-acids, varied considerably according both to the stage of development of the mould and to the composition of the nutrient medium. The *Aspergillus* withdrew ammonia from the nutrient solution, and synthesised from it amino-acids, polypeptides, and finally proteins. Inorganic phosphoric acid appeared in the mycelium even when the mould suffered from lack of phosphorus; it then played a limiting rôle in the mycelium. Soluble organic compounds of phosphorus were present in the mycelium in very variable amounts, and represented transitory products. The phosphorus present as protein was the most stable form of that element in the mycelium and varied the least in amount. The absorption of nitrogen from the nutrient medium, and its successive transformations in the mycelium depended to a large extent on the amount of phosphoric acid in the medium; these transformations were more uniform when the amount of phosphoric acid was small than when it was larger. At times, the increase in insoluble nitrogen and the increase in protein phosphorus ran parallel to each other during the growth of the mould. When the amount of phosphoric acid in the nutrient medium was decreased, the percentage of total phosphoric acid in the mycelium began to decrease, next became constant, and was then accompanied by a decrease in the amount of dry matter produced. The ratio of the protein phosphorus to the insoluble protein nitrogen varied within very wide limits according to the phosphoric acid content of the nutrient medium. The following amino-acids were isolated from the mycelium in the free state: alanine, leucine, tyrosine, and, probably, phenylalanine and proline. CHEMICAL ABSTRACTS.

Wood Decay. II. Enzyme Action in *Polyporus volvatus* Peck and *Fomes igniarius* (L.) Gillet. HENRY SCHMITZ (*J. Gen. Physiol.*, 1921, **3**, 795—801).—It is argued that *Polyporus volvatus* is parasitic. The cultures of *P. volvatus* and *Fomes igniarius* were prepared from the young sporophores and the fungi were examined for their enzymic activities. It was shown that *P. volvatus* contains the following enzymes: esterase, maltase, lactase, sucrase, raffinase, diastase, inulase, cellulase, hemicellulase, glucosidase, rennet, and catalase. *Fomes igniarius* contains urease as well as the above enzymes. S. S. Z.

Carbon Dioxide as a Fertiliser. FRENKEL (*Ann. Chim. analyt.*, 1921, [ii], **3**, 201—205).—Plants growing in a glass chamber absorbed carbon dioxide rapidly; in thirty minutes the amount of carbon dioxide in the atmosphere decreased from 5·2 to 2·0 parts

per 1000, and, after a further fifty minutes, to 0·26 part per 1000. An atmosphere containing a large proportion of carbon dioxide also increased the growth of plants (potatoes, lupins, and barley) by more than 200%, as compared with that of plants grown in the ordinary atmosphere. W. P. S.

The Mucilaginous Substances of *Laminaria flexicaulis*. (MME) Z. GRUZEWSKA (*Compt. rend.*, 1921, **173**, 52—54).—The mucilage of *Laminaria flexicaulis* contains at least two substances, of which one becomes soluble in the presence of salts. Under suitable conditions, the mucilage can be completely hydrolysed by successive treatments with acid, although it is probable that, during the hydrolysis, an unattackable complex is formed from a portion of the mucilage. W. G.

Constituents of *Lythrum salicaria*. J. R. CARRACIDO and A. MADINAVEITIA (*Anal. Fís. Quím.*, 1921, **19**, 148—151).—Purple loosestrife, *Lythrum salicaria*, has long been used in popular pharmacy as an astringent. In a study of the constituents of this plant, 1·4% of invert-sugar and 0·026% of choline were found. The presence of choline together with invert-sugar has also been noted in the Chenopodiaceæ, and is characteristic of maritime plants. This is confirmed in the case of *Lythrum* by the fact that sodium is present in the ash in greater quantities than potassium. Alkaloids of high molecular weight were absent. G. W. R.

Constituents of the Roots of *Rheum Emodi*, Webb. J. J. HOLMSTRÖM (*Schweiz. Apoth. Zeit.*, 1921, **59**, 169—175, 183—189; from *Chem. Zentr.*, 1921, iii, 43).—In the rhizomes of *Rheum Emodi*, Webb, the glucoside rhaponticin, chrysophanic acid, a small amount of emodin, a substance, probably rheochrysin, as well as dextrose, phytosterol, starch, and mucilage were found. *Rhaponticin*, $C_{21}H_{24}O_9$, forms small, highly refractive, rhombic tablets, m. p. 230—231°. A methoxyl determination gives the formula as $C_{20}H_{21}O_8$·OMe. *Acetylrhaponticin*, $C_{21}H_{18}O_9Ac_6$, forms colourless needles, m. p. 125°; it gives no colour with ferric chloride solution, a yellow colour with calcium chloride solution, and a blood-red colour, turning orange, with strong sulphuric acid. *Benzoylrhaponticin*, $C_{21}H_{18}O_9Bz_6$, forms a white varnish-like mass, m. p. nearly 110°. *Rhapontigenin*, $C_{15}H_{12}O_3$·OMe, forms colourless needles, m. p. 180—181°; its alcoholic solution gives a green colour with ferric chloride solution, and an orange-red colour with calcium chloride solution. *Acetylrhapontigenin*, $C_{16}H_{11}O_4Ac_4$, forms colourless prisms, m. p. 112°. *Benzoylrhapontigenin*, $C_{16}H_{11}O_4Bz_4$, forms colourless needles, m. p. 147°. A *compound*, $C_{22}H_{22}O_{10}$, probably rheochrysin, forms golden-yellow needles, m. p. 211°. G. W. R.

The Polyoses in Rotted Beetroots. ÉMILE VOTOČEK (*Bull. Soc. chim.*, 1921, [iv], **29**, 409—413).—The complex polyoses of rotted beetroots consist of lævulans accompanied by a small amount of glucosans, the relative proportions varying slightly with different samples. W. G.

Organic Chemistry.

Chemistry of the Heptane Solution. II. Revision of the Physical Constants of Heptane. E. KREMERS and R. KREMERS (*J. Amer. Pharm. Assoc.*, 1920, **9**, 860—864).—Fifteen specimens of the oleoresin of *Pinus sabiniana* were steam-distilled; the average yield was 7·8%. The distillates had d_{20} 0·685, except one which was 0·686. The crude heptane was purified by successive shaking with concentrated sulphuric acid, fuming sulphuric acid, sodium carbonate, and potassium permanganate. The constants of the purified heptane were n_{20} 1·3895; b. p. 97·33°/760 mm.; d_{20} 0·68288; γ_{20} 19·8 ergs; $[\alpha]_D$ 0. CHEMICAL ABSTRACTS.

The Labile Nature of the Halogen Atoms in Substituted Nitromethanes. ALEXANDER KILLEN MACBETH and DAVID DOIG PRATT (T., 1921, **119**, 1356—1361).

Ethyl Hydrogen Sulphate. HORACE BARRATT DUNNICLIFF and GERALD SNOWDEN BUTLER (T., 1921, **119**, 1384—1392).

Ultrafiltration of Lecithin Sols. H. BECHHOLD and S. M. NEUSCHLOSS (*Kolloid Zeitsch.*, 1921, **29**, 81—89).—The filtration of lecithin sols by ultra-filters under varying conditions has been investigated with the object of ascertaining the nature of lecithin emulsions. It is shown that a lecithin sol contains particles of very different sizes, and of these only the largest give rise to a turbidity which is recognisable by nephelometric methods. The quantity of the sol in a 1% solution recognisable by the nephelometer is 4% of the total amount. A portion of the lecithin is adsorbed by the filter when aqueous solutions are subjected to ultra-filtration; the quantity adsorbed becomes greater the greater the density of the filter. The slightly disperse lecithin particles are more strongly adsorbed than the highly disperse particles. In the ultrafiltration of lecithin emulsions the quantity of material which passes through the filter depends on the pressure under which filtration takes place, hence in the same filter by merely varying the pressure from 90 grams/cm.^{2} to 2000 grams/cm.^{2} it is possible to vary the filtrate from practically pure water to a solution which contains practically the whole of the lecithin. From this it is deduced that the surface tension at the interface water–lecithin is exceedingly small. The value has been calculated as less than 16 C.G.S. units. J. F. S.

The Quantitative Separation of the Lead Salts of the Saturated from the Less Unsaturated Fatty Acids. ARMIN SEIDENBERG (*J. Amer. Chem. Soc.*, 1921, **43**, 1323—1336).—The lead salts of the acids are dissolved in a mixture of the three solvents, alcohol, chloroform, and ethyl ether, and the two latter more

volatile and powerful solvents are evaporated off until all the more insoluble salts are precipitated. This process was found to give sharper and more easily controlled separations than the methods commonly used. By its use practically a complete removal of all the salts of the saturated acids can be obtained from their solutions and from the solvent used in washing the precipitate. Within wide limits, the results are independent of the amounts of the fatty acids used.

From oils or fats containing the more unsaturated acids it was not possible to obtain the saturated fatty acids in an approximately pure state by either the fractionation method or the lead salt–ether method. On the other hand, when only the less unsaturated acids, such as oleic acid, are present, the saturated fatty acids as isolated were found to have practically no iodine number and to be readily soluble in light petroleum. W. G.

Configuration of αα′-Dibromo-dibasic Acids. I. The Dibromoadipic Acids. Synthesis and Resolution of *trans-cyclo*Pentane-1 : 2 : 3-tricarboxylic Acid. WILLIAM HENRY PERKIN, jun., and ERIC ROBINSON (T., 1921, **119**, 1392—1399).

The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. II. Linolenic and Linolic Acids. SAMUEL COFFEY (T., 1921, **119**, 1408—1415).

Preparation of a Petrol from a Vegetable Oil. ALPHONSE MAILHE (*Compt. rend.*, 1921, **173**, 358—359).—When linseed oil is passed over a mixture of electrolytic copper and magnesium oxide as a catalyst at 550—650° and the product hydrogenated over reduced nickel, a mixture of aromatic and cyclic hydrocarbons is obtained. Benzene, toluene, xylene, *cyclo*hexane, and methyl*cyclo*hexane were identified. W. G.

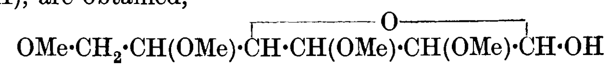
Production of Acetaldehyde from Acetylene. SOCIÉTÉ ANONYME DE PRODUITS CHIMIQUES (ETABLISSEMENTS MALÉTRA) (Brit. Pat. 140784).—In the preparation of acetaldehyde from acetylene, with an acid mercuric sulphate solution as catalyst, the process is rendered practically continuous by the periodic addition of ferric oxide to the bath. For example, 9·26 kilos. of mercury are triturated with 7·4 kilos. of ferric oxide and 70 kilos. of concentrated sulphuric acid; 191 kilos. of water are added, and the mixture is heated to 70—83°, preferably about 80°. Acetylene is admitted to the catalytic liquid thus prepared, and water is added from time to time equivalent to the amount of acetaldehyde produced, so that the concentration of the sulphuric acid is maintained at 30—35% of the total catalytic liquid. After 280 kilos. of acetaldehyde have been obtained, a further 7·4 kilos. of ferric oxide and 13·34 kilos. of sulphuric acid are added and the operation may be repeated to an almost unlimited extent. In practice, after about ten operations, it is desirable to decant the liquid from the

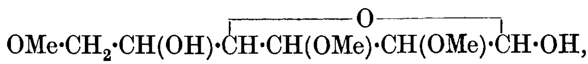
small quantity of tarry matter formed. It is essential that the acetylene be purified before use, particularly from hydrogen phosphide. G. F. M.

Structure of Cellobiose. M. BERGMANN (*Naturwiss.*, 1921, **9**, 308—309; from *Chem. Zentr.*, 1921, iii, 214; cf. this vol., i, 307).—Cellobial, which is structurally identical with glucal, has in the reducing half of the molecule a double linking between carbon atoms 1 and 2 and an " oxygen bridge " between 1 and 4; the hydroxyl group in position 3 is not substituted. Since the carbon atom 6 does not take part in the formation of a disaccharide, and since in the formation of cellobial from cellobiose displacement of the glucosidic attachment does not occur, the formula for cellobiose must be $OH\cdot CH_2\cdot CH(O\cdot C_6H_{11}O_5)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot OH$.

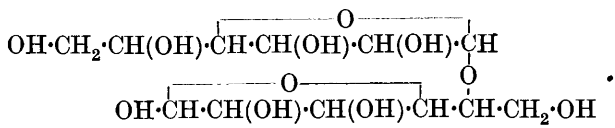
G. W. R.

Constitution of Starch and Glycogen. P. KARRER (*Naturwiss.*, 1921, **9**, 399—403; from *Chem. Zentr.*, 1921, iii, 214; cf. this vol., i, 310—313).—A summary of earlier work. By acid hydrolysis of heptamethyl methylcelloside, *tetramethylglucose* (I), and *trimethyl glucose* (II), are obtained,

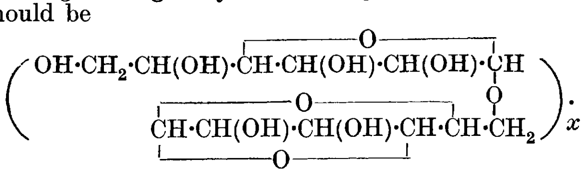
(I.) 

(II.) 

whereby the formula for cellobiose must be (III),

(III.) 

The analogies in the behaviour of starch and α-amylose extend to their reactions with alkaline-earth hydroxides. *α-Octamylose* gives a precipitate with barium hydroxide solution. A similar compound is obtained with α-tetra-amylose and may be precipitated by addition of a little ethyl alcohol. α-Tetramylose by distillation in a vacuum gives a good yield of *lævoglucosan.* The formula for starch should be



The position of the anhydride bridge is undetermined.

G. W. R.

Plant Colloids. XI. Electro-disintegration of Starch Solutions. M. SAMEC and ANKA MAYER (*Koll. Chem. Beihefte*, 1921, **13**, 272—288; cf. this vol., i, 400).—By electro-disintegration

of starch solutions, a retrograded solution of amyloses was obtained. This solution yields a blue coloration with iodine (amylo-amylose), has $\alpha_D + 189°$, and a mean molecular weight of about 80,000. This fraction constitutes 17% of the starch substance; it is electro-neutral and corresponds with Maquenne's amylose. The amylopectin which has thus been separated from the amylo-amyloses yields a reddish-violet colour with iodine. In 2% solution, it has an electrical conductivity $8{\cdot}3 \times 10^{-5}$ and a hydrogen-ion concentration $2{\cdot}4 \times 10^{-4}N$. It has a mean molecular weight of 113,000. By heating amylopectin with water in neutral solution under pressure, non-retrograded erythroamyloses are formed. These give a wine-red coloration with iodine, have $\alpha_D + 195—196°$, and a mean molecular weight of about 130,000—140,000. In solution with its own acid reaction, amylopectin is not only hydrolysed but also disaggregated and yields within six hours 80% of dialysable products. The colloidal residue from this has a mean molecular weight of 57,000, but the iodine coloration and the optical rotation are the same as those of the erythroamyloses above. The presence of erythroamyloses in solution is substantiated colorimetrically. From the change in the iodine coloration with increasing addition of iodine the quantity relationship of the iodine–amyloamylose complex is deduced as $(C_6H_{10}O_5)_2I$. The erythroamyloses appear to take up a larger quantity of iodine. The name "soluble starch" for the erythroamyloses is justified. The "elementary molecule" of starch may possibly have a molecular weight below 2000. J. F. S.

Constitution of "Iodide of Starch." A. LOTTERMOSER (*Zeitsch. angew. Chem.*, 1921, **34**, 427—428).—From the results of electric-potential and other physical measurements, the author concludes that the supposition of Biltz and others that the so-called "iodide of starch" is an adsorption compound of starch and molecular iodine is justified. Neither iodion nor potassium iodide is adsorbed by starch to any appreciable extent, but experiments indicated that in $N/100$ or less potassium iodide solutions there is a noticeable adsorption of tri-iodion. In $N/10$- or $N/5$-solutions, this is, however, so small as to be negligible. In general, the results confirmed the statement of Mylius that for the formation of the blue colour the presence of iodion is necessary, since it participates, if only very temporarily, in the adsorption. G. F. M.

Wood Cellulose. EMIL HEUSER and E. BOEDEKER (*Zeitsch. angew. Chem.*, 1921, **34**, 461—464).—Contrary to the views of Cross and Bevan and others, the authors suggest the hypothesis that all plant cellulose, from whatever source derived, is a chemical individual, and that there is only one variety of cellulose, namely, that expressed by the formula $(C_6H_{10}O_5)_n$. It has already been shown (Heuser and Haug, *Zeitsch. angew. Chem.*, 1918, **31**, 99) that purified straw cellulose is identical with cotton cellulose and the identity of wood cellulose, suitably purified from pentosans, etc., with the latter is now demonstrated. A bleached wood cellulose was freed from resin and fat by extraction with a mixture of benzene and alcohol,

and was then extracted three times with boiling 6% sodium hydroxide (or alternatively with cold 17% sodium hydroxide) whereby the pentosan content was reduced from 4·06% to 1·8—1·92%. At the same time both the ash and the copper number were reduced, the latter from 4·07 to 0·8—0·9. The pentosan remains therefore the only appreciable impurity, and by sufficiently repeated alkali extraction this can be eliminated to such an extent that on distillation with 12% hydrochloric acid by Tollens and Kröber's method no furfuraldehyde is obtained, although of course there is considerable loss in cellulose by this treatment. The hydrolysis of the wood cellulose purified as above by triple alkali extraction was compared with that of cotton cellulose, dextrose being estimated periodically both by copper reduction and polarimetrically. The hydrolysis was carried out in cold concentrated hydrochloric acid by Willstätter and Zechmeister's method. In each case the maximum glucose reading was reached in 16·5 hours, and about 97·5% was obtained, showing that the course of the hydrolysis was with both cellulose preparations identical. Further, from the wood cellulose hydrolysis 94·2% of pure dextrose was actually isolated and identified by its osazone. G. F. M.

Nature of the Swelling Process. II. E. KNOEVENAGEL and ROBERT MOTZ (*Koll. Chem. Beihefte*, 1921, **13**, 233—241; cf. this vol., i, 402).—Partition experiments between swollen cellulose acetate hydrogel and aqueous solutions of aniline, phenol, methyl tartrate, and ethyl tartrate of small concentrations have been carried out at 18° and 30—33°, both acetone-soluble and chloroform-soluble cellulose acetate being used in the experiments. It is shown that a partition occurs after twenty-four hours in keeping with Henry's law. The establishment of such an equilibrium points to the occurrence of a process of solution in both phases; that is, no adsorption takes place in the swollen cellulose acetate. Special experiments in the case of ethyl tartrate show that unswollen cellulose acetate does not remove any of the ester from its aqueous solution in short periods of time, exactly in the same way as it was previously shown (*loc. cit.*) that unswollen cellulose acetate in aqueous solutions of dyes remains completely uncoloured. That is, only after months or years does unswollen cellulose acetate come into equilibrium with the dye solution, whilst swollen cellulose acetate, under similar conditions, and according to the extent of the swelling, attains an equilibrium with the dye solution in a few minutes or hours and is dyed in full colours. J. F. S.

Nature of the Swelling Process. III. E. KNOEVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, **13**, 242—261; cf. preceding abstract).—The swelling of various kinds of cellulose acetate in binary mixtures of alcohol with benzene, nitrobenzene, and carbon tetrachloride respectively has been measured at ordinary temperatures, as well as the surface tension of all four solvents, and the binary mixtures named above. The degree of swelling of cellulose acetate in the four simple solvents decreases in the order: nitrobenzene, benzene, alcohol, carbon tetrachloride,

so that of these only nitrobenzene can be regarded as a strong swelling medium for cellulose acetate; carbon tetrachloride acts very slightly in this respect. The surface tension of the four solvents falls in the order: nitrobenzene, benzene, carbon tetrachloride, alcohol. In the binary mixtures, the alcohol lowers the capillarity of the other constituent. The amount of lowering of the capillarity is greatest for the first addition of the second constituent and is greater the greater the difference between the surface tension of alcohol and that of the second constituent. A qualitative relationship between the lowering of the surface tension and the degree of swelling in the binary mixtures has been established. The stronger the capillary action of the alcohol, the more does the degree of swelling increase. The action of the alcohol, however, is in opposition to the swelling action of the other component; consequently there exists for each binary mixture a composition which gives an optimum swelling effect. J. F. S.

Nature of the Swelling Process. IV. Swelling and Internal Friction in the System Cellulose Acetate–Nitrobenzene–Alcohol. E. KNOEVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, **13**, 262—271; cf. preceding abstracts.)—The viscosity of solutions of various concentrations of cellulose acetate in mixtures of nitrobenzene and ethyl alcohol containing 90, 70, and 50 vol.% respectively of the former substance has been measured at 25°; the specific gravity of all the solutions has also been determined. It is shown that the viscosity curve for the weaker swelling liquid always lies below that of the stronger swelling liquid. The ratio of the viscosities of any two equally concentrated cellulose acetate solutions in different mixtures of nitrobenzene and alcohol is constant for all concentrations of cellulose acetate. The viscosity of a given binary mixture increases with increasing cellulose acetate concentration, and is approximately proportional to the logarithm of the internal friction. J. F. S.

Cellulose. IV. Depolymerisation of Ethylcellulose. KURT HESS, WALTER WITTELSBACH, and ERNST MESSMER (*Zeitsch. angew. Chem.*, 1921, **34**, 449—454; see this vol., i, 401).—Trustworthy conclusions as to the constitution of cellulose from the products of the acetolysis of alkylated celluloses can only be drawn when alkylation has been conducted in such a way as to exclude the probability of the disruption of glucoside or ether-like linkings. Under these conditions, the limit of alkylation is reached when two ethyl groups per $C_6H_{10}O_5$ have been taken up. The resulting diethylcellulose is an individual substance and when subjected to acetolysis depolymerisation occurs with the absorption of one acetyl group for each $C_6H_8O_3(OEt)_2$, and without the generation of a free aldehyde group. The acetylated product is easily hydrolysed by methyl alcoholic ammonia and gives a product of the same empirical composition as the original material and with a molecular weight in dilute solution of 800—900, rapidly increasing with increasing concentration owing to association. This substance therefore contains at most four hexose residues, and since free

aldehyde groups are absent it must be assumed that these structural units are held together in the original cellulose molecule by some other means than a "glucoside" linking. Although approximately identical molecular weights were found for different preparations of the substance, differences in optical rotation and melting point exclude the possibility of their absolute identity, and indicate that the depolymerisation is accompanied by isomerisation. Further acetolysis results in the formation of ethylated acetyl-hexoses which on hydrolysis give a syrup which appeared to be mainly a mixture of triethyl- and diethyl-glucose, the latter preponderating, although only the former has yet been isolated in crystalline form. The presence or otherwise of other ethylated glucoses in the syrup and its actual percentage composition are still to be determined, but the results so far do not show complete agreement with those of either Denham and Woodhouse (T., 1921, **119**, 77) or Irvine (T., 1920, **117**, 1489). G. F. M.

Are Hydrocelluloses Simple Substances? H. Ost and R. Bretschneider (*Zeitsch. angew. Chem.*, 1921, **34**, 422—423).—From evidence obtained by a comparative examination of hydrocellulose, made by Girard's method, and cellulose, purified as for nitration purposes, before and after digestion with boiling lime-water containing 0·5—1·0% of calcium oxide, the authors draw the conclusion that hydrocelluloses are simple substances and are not mixtures of cellulose and cellulose dextrins as suggested by Hauser and Herzfeld, and by Schwalbe and Becker (cf. A., 1915, i, 941; 1920, i, 474).

The hydrocellulose and cellulose contained 0·24—0·34% and 0·30% of ash, and 3·17—3·94% and 5·39% of moisture respectively, and during their digestion in boiling lime-water for twelve hours 24·4% of hydrocellulose and 15·8% of cellulose dissolved. At the same time, the "copper numbers" of the hydrocellulose and cellulose changed from 6·69 to 0·91 and 2·05 to 0·61, and the "cellulose numbers" from 0·14 to 0·29 and 0·30 to 0·36 respectively.

Although the "copper" and "cellulose" numbers of the final residues from hydrocellulose and cellulose are similar, the hydrocellulose residue is essentially different from cellulose and is similar to the original hydrocellulose. This is shown by the viscosity of its solution in cuprammonium hydroxide solution and the solubility of its acetate (acetylation is carried out by means of acetic acid, acetic anhydride, and zinc chloride as catalyst) in acetone. [See, further, *J. Soc. Chem. Ind.*, 1921, 654A.] A. J. H.

Pseudo-bases. III. Dialkylaminomethyl Alkyl Ethers and Sulphides. Charles Maxwell McLeod and Gertrude Maud Robinson (T., 1921, **119**, 1470—1476).

Derivatives of some Amino-acids. L. Hugounenq and G. Florence (*Bull. Soc. Chim. Biol.*, 1921, **3**, 283—285).—A description of the action of chromium hydroxide on aqueous solutions

of some amino-acids, and of the preparation of double salts by the action of calcium hydroxide on the hydrochlorides of aspartic acid and glycine. C. R. H.

The Constitution of the Nitroprussides. II. Alkylation of Nitroprussic Acid. GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1921, **119**, 1450—1452).

Manufacture of Hydrocarbons [Naphthenes]. CHARLES WEIZMANN and DAVID ALLISTON LEGG (Brit. Pat. 165452).—A mixture of naphthenes is obtained by polymerising by means of aluminium chloride the mixture of butylenes obtained by the dehydration of *n*-butyl alcohol. In carrying out the process the vapour of *n*-butyl alcohol is passed at atmospheric pressure through a tube containing pumice coated with aluminium oxide heated at 250—320°, when a mixture of β- and α-butylene is formed containing about 80% of the former. At higher temperatures, for example, 360—390°, the product is practically all β-butylene, and the yield nearly theoretical. The liquefied butylene is then treated with anhydrous aluminium chloride in the proportion of 28 grams of the former to 0·5 gram of the latter and the temperature is kept below −10°. If an autoclave is used a temperature as high as 15° is admissible. Polymerisation is complete in about two hours and a practically quantitative yield of naphthenes is obtained, distilling as follows: 8 grams at 260—290°/17 mm., 13 grams at 270—350°/17 mm., and 5 grams above 350°/17 mm. G. F. M.

Nitration of Toluene. M. GIUA (*Gazzetta*, 1921, **51**, ii, 113—115).—The author expresses agreement with Drew's statement (T., 1920, **117**, 1615; cf. also Brady and Taylor, T., 1920, **117**, 876) that the compound, m. p. 79·5°, isolated from the oily residues obtained in the purification of 2 : 4 : 6-trinitrotoluene is not the 2 : 3 : 6-compound, as supposed by Molinari and Giua (A., 1915, i, 790), but an additive compound of 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes.

Doubt is cast on Drew's statement (*loc. cit.*) that 2 : 3 : 6-trinitrotoluene is formed when toluene is nitrated directly. Drew isolated this compound by treating the mixed products with hydrazine hydrate, which reacts with the 2 : 3 : 4- and 3 : 4 : 6-compounds, but leaves the 2 : 3 : 6-compound unaltered. The author finds, however, that the 2 : 3 : 6-compound should be easily attacked by hydrazine hydrate under the conditions employed by Drew, so that the latter's so-called 2 : 3 : 6-compound is probably the 2 : 3 : 4-compound, these two having the same melting point.

[The author gives Drew's name throughout this paper as Barry.] T. H. P.

Reduction of Trinitroluene. ELIAS BIELOUSS (Brit. Pat. 166934; addition to 137529).—The process of reducing trinitrotoluene to triaminotoluene by means of iron and hydrochloric acid, as described in the earlier patent, is improved by using only a small quantity of hydrochloric acid as in the technical

reduction of nitrobenzene. The iron compounds are thus obtained as a sludge which can be removed by filtration from the triaminotoluene solution. In the example given, the quantities suggested are 230 kilos. of trinitrotoluene, 700 kilos. of iron turnings, 800 litres of water, and 20 litres of 35% hydrochloric acid, the reaction mixture being maintained at 60—80°. Triaminotoluene serves as a dye for cotton, silk, and wool, as a photographic developer, and as an intermediate. G. F. M.

9 : 10-Dihydrophenanthrene. HERBERT HENSTOCK (T., 1921, **119**, 1461—1463).

Influence of Substituents on Reactions. VI. Nitration of Substituted Acetanilides. HARTWIG FRANZEN and ERWIN ENGEL (*J. pr. Chem.*, 1921, **102**, 156—186).—The nitration of acetanilide and its *o*-methyl-, *o*-chloro-, *o*-bromo-, *o*-ethoxy-, and *m*-chloro-derivatives has been investigated. In general, the finely-divided acetanilide (33·75 grams) is gradually added to a well-stirred mixture of fuming nitric acid (*d* 1·505, 65 c.c.) and glacial acetic acid (35 c.c.) which is cooled in a freezing mixture, the rate of addition being so regulated that the temperature does not exceed 0°. The product is allowed to remain in the cooling mixture during twelve hours so that it gradually attains the atmospheric temperature; it is then poured into water (350 c.c.) and the precipitate is collected and dried. Under these conditions, nitration is complete except in the cases of *o*-bromo- and *m*-chloro-acetanilide, for which reaction must be continued during twenty-four hours. In certain cases, the method of Witt and Utermann (A., 1907, i, 27), which involves the use of nitric acid, glacial acetic acid, and acetic anhydride, has also been employed. In this manner, the nitrated anilide is not quantitatively precipitated, but the losses are shown to be distributed in general uniformly over the various isomerides. The quantitative separation of the *o*- and *p*-isomerides is effected by the Witt-Utermann method (*loc. cit.*), the necessary corrections being worked out experimentally for the individual cases.

The authors are led to the following conclusions. The introduction of methyl, chlorine, or bromine in position 2 and of chlorine in position 3 of acetanilide increases the ease of replacement of the hydrogen atom in position 6 by nitric acid and diminishes that of the hydrogen atom in position 4; in this respect, bromine has a less marked action than chlorine or methyl, which have approximately the same effect. The introduction of the ethoxy-group in the 2-position of acetanilide so greatly diminishes the reactivity of the hydrogen atom in position 6 towards nitric acid that the *o*-nitro-derivative is not produced; the replaceability of hydrogen atom 4 is likewise diminished, whilst that of atom 3 is very markedly increased. The addition of ammonium nitrate to the nitrating mixture of nitric acid and glacial acetic acid causes an alteration in the relative amounts of the isomerides produced. In the nitration of acetanilides with nitric and acetic acids and acetic anhydride compared with the action in the absence of the latter, a displace-

ment of the relative quantities of the isomerides is observed of such a kind that the directive action of the acetylamino-group is more pronounced.

The following compounds have not been described previously: 2-*chloro*-6-*nitroacetanilide*, yellow needles, m. p. 130—132°; 2-*chloro*-6-*nitroaniline*, yellow needles, m. p. 76°; 2-*bromo*-6-*nitroacetanilide*, yellow needles, m. p. 190°. H. W.

The Method of Witt and Utermann for the Separation of *o*- and *p*-Nitroacetanilides. HARTWIG FRANZEN and FRITZ HELWERT (*J. pr. Chem.*, 1921, **102**, 187—193).—Witt and Utermann (A., 1907, i, 27) have described a process for the separation of *o*- and *p*-nitroacetanilides which depends on the solubility of the former and the insolubility of the latter in a mixture of potassium hydroxide solution (50%, 1 vol.), water (4 vols.), and alcohol (1 vol.) at 0°. The applicability of the method to other nitroacetanilides has now been investigated. All the *o*-nitroacetanilides dissolve in the mixture with greater or less readiness; on the other hand, certain para-derivatives are very appreciably soluble. In general, it is shown that *m*-nitroacetanilides can be separated in this manner from the ortho-derivatives, but this case is likely to be encountered seldom in practice. In the majority of instances, *p*-nitroacetanilides can be separated from the corresponding ortho-compounds; exceptions are, however, to be expected with the halogenated *o*-nitroacetanilides. In the naphthalene series, the separation of 2- and 4-nitroacetonaphthalides is improbable, but 1-nitro-β-acetonaphthalide should be separable from the other nitro-β-acetonaphthalides. A further limitation to the applicability of the method is probably imposed by the sparing solubility of certain *o*-nitroacetylamino-compounds in the solution.

The volume of the mixture necessary for the solution of one gram of the various anilides at 0° is shown by the figures in parenthesis: *o*-nitroacetanilide (20), 6-nitro-*o*-acetotoluidide (40), 2-nitro-*p*-acetotoluidide (83), 1-nitro-β-acetonaphthalide (52), 2-nitro-α-acetonaphthalide (150), 4-nitro-α-acetonaphthalide (312). In certain cases, at any rate, it is possible to replace potassium hydroxide by sodium hydroxide, but not by ammonia. H. W.

Amines. IX. Alkylation of Aromatic Amines by Heating with Aliphatic Alcohols. ARTHUR J. HILL and JOHN J. DONLEAVY (*J. Ind. Eng. Chem.*, 1921, **13**, 504—509; see A., 1920, i, 671).—The formation of tertiary bases by heating isomeric toluidines with ethyl alcohol or *n*-butyl alcohol was investigated and found to be promoted by certain catalysts (cupric chloride, sodium bromide, and calcium chloride) and by the use of a large excess of the alcohol. The mixtures were heated at 175° to 180° for eight hours. The yields varied from 50% in the case of di-*n*-butyl-*o*-toluidine to 90% for diethyl-*p*-toluidine; *o*-toluidine was the least reactive of the isomerides. Two new amines were prepared by the method, *di*-n-*butyl*-o-*toluidine*, b. p. 256—258°/755 mm., and *di*-n-*butyl*-m-*toluidine*, b. p. 278—280°/755 mm. W. P. S.

Preparation of Dibenzylaniline-4 : 4′-disulphonic Acid and Ethylbenzylaniline-4′-sulphonic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 87882 and 87883; from *Chem. Zentr.*, 1921, iv, 259).—*Dibenzylaniline*-4 : 4′-*disulphonic acid*,

$$NPh(CH_2·C_6H_4·SO_3H)_2,$$

is prepared by the condensation of two molecules of sodium ω-chlorobenzyl-*p*-sulphonate with one molecule of aniline in aqueous solution. *Benzylethylaniline*-4′-*sulphonic acid*, $NEtPh·CH_2·C_6H_4·SO_3H$, is similarly prepared by condensation of sodium ω-chlorobenzyl-*p*-sulphonate with monoethylaniline. G. W. R.

Phototropy. PATRICK GALLAGHER (*Bull. Soc. chim.*, 1921, [iv], **29**, 683—696).—From a study of a number of salicylideneamines the author was not able to trace any direct relationship between phototropy and chemical constitution. The changes in colour are not to be attributed to purely chemical changes in the molecule. The salicylideneamines were prepared by condensation in alcoholic solution and the following are described.

Salicylidenenitro-ψ-cumidine, $OH·C_6H_4·CH:N·C_6HMe_3·NO_2$, m. p. 120°, is not phototropic. *Salicylidene-α-chloro-β-naphthylamine*, $OH·C_6H_4·CH:N·C_{10}H_6Cl$, m. p. 156°, is slightly phototropic. *Salicylidene*-o-*aminocinnamic acid*, $OH·C_6H_4·CH:N·C_6H_4·CH:CH·CO_2H$, m. p. 231°, is phototropic. *Salicylidene*-p-*phenetidine*, m. p. 94°, is not phototropic. *Salicylidene*-p-*aminobenzaldehyde*, m. p. 99°, is not phototropic. *Salicylidene*-p-*aminoazobenzene*,

$$OH·C_6H_4·CH:N·C_6H_4·N:NPh,$$

m. p. 156°, is not phototropic. *Disalicylidene*-2 : 4-*diaminoazobenzene*, $NPh:N·C_6H_3(N:CH·C_6H_4·OH)_2$, m. p. 150°, is not phototropic. Ethyl salicylidene-*p*-aminobenzoate is phototropic, but the methyl ester is not. *Salicylidene*-1 : 2 : 4-*nitrotoluidine*, m. p. 129°, is thermotropic, but not phototropic. *Salicylidene*-1 : 3 : 6-*nitrotoluidine*, m. p. 125°, is not phototropic. *Salicylidene*-1 : 4 : 2-*nitrotoluidine*, m. p. 112°, is very thermotropic, but not phototropic. *Disalicylidene*-p : p-*diamino*-m : m-*dimethyldiphenyl*,

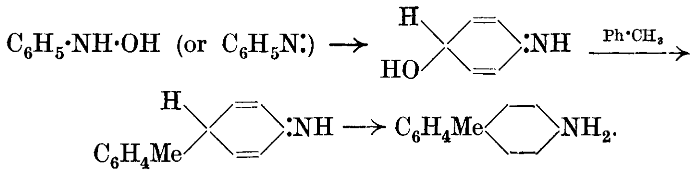
$$(OH·C_6H_4·CH:N)_2C_{12}H_6Me_2,$$

m. p. 203°, is thermotropic, but not phototropic. *Salicylidene*-1 : 2-*naphthalenediamine*, $OH·C_6H_4·CH:N·C_{10}H_6·NH_2$, m. p. 162°, is not phototropic. *Disalicylidenenaphthalene*-1 : 2-*diamine*, m. p. 213°, the -1 : 4-*diamine*, m. p. 142°, the -1 : 5-*diamine*, m. p. 220°, the -1 : 8-*diamine*, m. p. 199°, and the -2 : 7-*diamine*, m. p. 203°, are not phototropic. *Salicylidene*-o-*phenylenediamine*, m. p. 90°, is very phototropic at low temperatures, but it having been shown by Senier and Shepheard (T., 1909, **95**, 441, 1943) that the disalicylidene derivative is not phototropic, the monosalicylidene derivative was condensed with a number of aldehydes; in no case, however, was phototropy observed. *Benzylidenesalicylidene*-o-*phenylenediamine*, $OH·C_6H_4·CH:N·C_6H_4·N:CHPh$, has m. p. 244°; m-*tolylidenesalicylidene*-o-*phenylenediamine* has m. p. 238°; p-*tolylidenesalicylidene*-o-*phenylenediamine* has m. p. 135°; *salicylideneanisylidene*-o-*phenylenediamine* has m. p. 130°; *salicylidenepiperonylidene*-o-

phenylenediamine has m. p. 140°; and *salicylidene*-m-*methoxysalicylidene*-o-*phenylenediamine* has m. p. 125°.

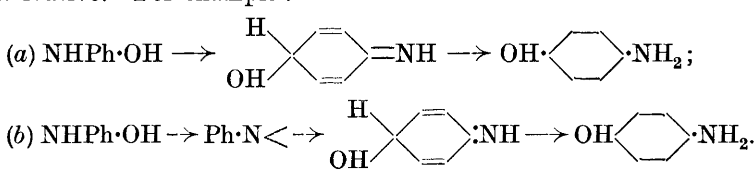
Benzylamine condenses with nitrosobenzene in alcoholic solution to give a red oil, which is apparently *s*-phenylbenzyldiazine; when this substance is reduced with zinc and alcoholic sodium hydroxide it yields *s*-phenylbenzylhydrazine, m. p. 35—36°. W. G.

Transformation of certain Aromatic Compounds. E. BAMBERGER (*J. pr. Chem.*, 1921, **102**, 267—275).—In order to explain the production of 4-*p*-aminophenyltoluene (Bamberger, A., 1895, i, 289; Kühling, *ibid.*, i, 182) by the action of aluminium chloride on a mixture of phenylhydroxylamine and toluene, Kliegl and Huber (A., 1920, i, 835) have assumed the intermediate production of the residue, $-C_6H_4 \cdot NH-$. According to the author, the reaction can be readily explained by the annexed scheme, which has been applied previously to similar cases:

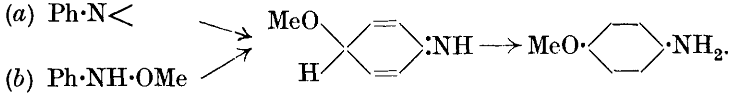


This conception has the advantage that it can be applied to a large number of other cases, such as the transformation of azoxybenzene to *p*-hydroxyazobenzene or benzeneazodiphenyl, of nitrobenzene to *o*-nitrosophenol, of phenylnitroamine to *o*-nitroaniline, of α-naphthylnitroamine to β-naphthaquinone-α-diazide, of dimethylaniline oxide to *o*-dimethylaminophenol, of nitrosomethylaniline to *p*-nitrosomonomethylaniline, and of phenylsulphamic acid to *o*-anilinesulphonic acid. H. W.

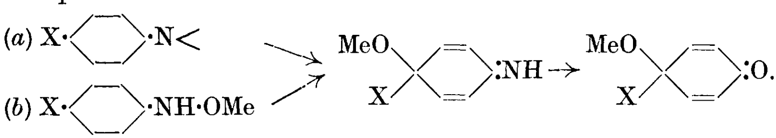
Arylhydroxylamines and Arylazides. A Comparison. EUGEN BAMBERGER (*Annalen*, 1921, **424**, 233—296).—A general review of the chemistry of the arylhydroxylamines, especially from the point of view of the mechanism whereby, under the influence of various reagents, transformations occur which involve substitution in the nucleus. Eight typical reactions are discussed, and it is shown that in every case at least two alternative mechanisms are possible. These are (*a*) that isomeric change occurs to an imino-ψ-quinol, which, provided the necessary hydrogen atom is present, passes into the benzenoid form, (*b*) that water is eliminated with the formation of an arylimide, Ar·N<, which then takes up the elements of water (or of the reagent), forming the same quinonoid derivative. For example:



The author considers the second mechanism to be the more probable, one reason being that it avoids the necessity for supposing that when, for instance, a mixture of methyl alcohol and sulphuric acid acts on a hydroxylamine, a methoxy-group wanders from a methoxylamine residue initially formed :



The same holds in the case of para-substituted arylhydroxylamines, in which rearrangement from the quinonoid to the benzenoid form is impossible :



The products in this case are the ethers of ψ-quinols or of imino-ψ-quinols.

With the view of obtaining more light on these questions, the behaviour towards various reagents of certain arylhydroxylamines and arylazides have now been examined comparatively, particular attention being directed to the relative quantities of the various products formed. This was essential, because, whilst the undoubted qualitative similarity between the two sets of reactions might be traceable to the production in each case of the arylimide,

$$\mathrm{Ar{\cdot}NH{\cdot}OH} \xrightarrow[(-\mathrm{H_2O})]{} \mathrm{Ph{\cdot}N}< \xleftarrow[(-\mathrm{N_2})]{} \mathrm{Ar{\cdot}N_3},$$

an alternative hypothesis had been suggested by Friedländer and Zeitlin (A., 1894, i, 184), namely, that the azide first passed into the hydroxylamine. This (according to Friedländer and Zeitlin) is why Griess obtained *p*-aminophenol from phenylazide by the action of dilute sulphuric acid (A., 1886, i, 459).

The following is a summary of the comparative experiments : (1) (Cf. A., 1912, i, 691.) Phenylhydroxylamine (20 grams) and dilute sulphuric acid (1 : 10), heated for forty-five minutes on a water-bath, gave *p*-aminophenol (14 grams), *p*-aminophenol-*o*-sulphonic acid (0·5 gram), and azoxybenzene (2 grams). (1*a*) * Phenylazide (10 grams) and dilute sulphuric acid (1 : 3 by volume), boiled for twenty-four hours, gave *p*-aminophenol (1 gram) and *p*-aminophenol-*o*-sulphonic acid, but no azoxybenzene. (2) (*ibid.*) Phenylhydroxylamine (6 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), boiled for five minutes, gave *p*-amino-*p*′-hydroxydiphenyl (0·8—0·9 gram), aniline, azoxybenzene (?), and amphoteric matter, m. p. about 179°. (2*a*) * Phenylazide (6 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), boiled for one and three-quarter hours, gave *p*-amino-*p*′-hydroxydiphenyl (0·4 gram), *p*-hydroxydiphenylamine (trace), aniline (doubtful trace), and amphoteric

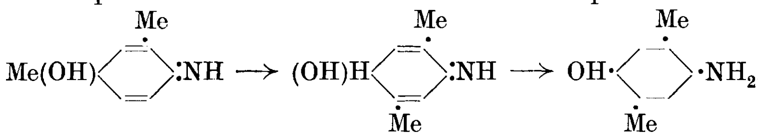
* Denotes reactions which have not previously been qualitatively investigated.

matter, m. p. about 182°, but no azoxybenzene. (3) (Cf. A., 1894, i, 520.) Phenylhydroxylamine (100 grams), alcohol (2400 c.c.), and sulphuric acid (50 c.c.) after twenty-six hours on the water-bath, gave *p*-phenetidine (45 grams), *o*-phenetidine (8 grams), *p*- and *o*-aminophenol (3·5 grams), aniline (4 grams), azoxybenzene (14 grams), and *p*-aminodiphenylamine (very little). (3*a*) * Phenylazide (15 grams), ethyl alcohol (105 c.c.), and sulphuric acid (52 c.c.), after twenty-five hours on the water-bath, gave *p*-phenetidine (5·5 grams), *o*-phenetidine (0·3 gram), *p*-aminophenol (0·5 gram), aniline (0·4 gram), *p*-aminodiphenylamine (very little), and phenol (by odour only), but no azoxybenzene. (3)′ * Phenylhydroxylamine (100 grams), methyl alcohol (2400 c.c.), and sulphuric acid (50 c.c.), after eight hours on the water-bath, gave *p*-anisidine (21 grams), *o*-anisidine (6 grams), *p*-aminophenol (0·2 gram), *p*-aminophenol-*o*-sulphonic acid, aniline (small quantity), azoxybenzene (17 grams), and much gum. (3′*a*) * Phenylazide (5 grams), methyl alcohol (50 c.c.), and sulphuric acid (25 grams), after twenty-two hours on a water-bath, gave *p*-anisidine (1·9 grams,) (probably) *o*-anisidine and aniline (0·4 gram together), *p*-aminophenol, but no azoxybenzene. (4) (Cf. following abstract.) Phenylhydroxylamine (60 grams) and concentrated hydrochloric acid (saturated at 0°), after thirty days at 0°, gave *p*-chloroaniline (37 grams), *o*-chloroaniline (15 grams), *op*-dichloroaniline (0·2 gram), azoxybenzene (0·2 gram), and doubtful traces of aniline, *o*-aminophenol, and *s*-trichloroaniline. (4*a*) (Cf. A., 1886, i, 459.) Phenylazide (131 grams) and concentrated hydrochloric acid, first at 0° and finally on the water-bath, gave *p*-chloroaniline (86 grams), *o*-chloroaniline (25 grams), *op*-dichloroaniline (0·3 gram), and aniline (0·2 gram), but no azoxybenzene. (5) *o*-Tolylhydroxylamine * (34 grams), methyl alcohol (1000 c.c.), and sulphuric acid (17 c.c.), after thirty days at room temperature, gave 5-methoxy-*o*-toluidine (13 grams), 6-amino-*m*-cresol (0·2 gram), and azoxytoluene (0·7 gram). (5*a*) * *o*-Tolylazide (20 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after twenty-four hours in the cold and subsequent heating on the water-bath, gave 5-ethoxy-*o*-toluidine (4·8 grams), 6-amino-*m*-cresol (1·2 grams), and a small quantity of phenolic material, but no azoxytoluene. (6) * *o*-Tolylhydroxylamine (61 grams) and dilute sulphuric acid (1 : 10 by volume), after forty-five minutes on the water-bath, gave 6-amino-*m*-cresol (20·4 grams), *o*-toluidine (1·3 grams), and azoxytoluene (7 grams). (6*a*) *o*-Tolylazide and sulphuric acid gave 6-amino-*m*-cresol (cf. Friedländer and Zeitlin, *loc. cit.*). (7) (Cf. following abstract.) *o*-Tolylhydroxylamine (30 grams) and concentrated hydrochloric acid (saturated at 0°) after thirty days at winter temperatures gave 5-chloro-*o*-toluidine (13 grams), 3-chloro-*o*-toluidine (0·3 gram), 4-chloro-*o*-toluidine (1 gram), and azoxytoluene (0·2—0·3 gram). (7*a*) * *o*-Tolylazide (120 grams) and concentrated hydrochloric acid (saturated at 0°), after eight days in the cold, gave 5-chloro-*o*-toluidine (100—110 grams), 3-chloro-*o*-toluidine, but no azoxytoluene. (8) * *m*-Tolylhydroxylamine (30·7 grams), ethyl alcohol (900 c.c.), and sulphuric acid (15 c.c.), after keeping for fifteen days in the dark,

gave 6-ethoxy-*m*-toluidine (3·7 grams), 5-amino-*o*-cresol (very little), and azoxytoluene (3·4 grams). (8*a*) * *m*-Tolylazide (10 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after three days' keeping in the cold and fifteen hours' subsequent heating on the water-bath, gave 6-ethoxy-*m*-toluidine (1·4 grams), 5-amino-*o*-cresol (2·5 grams), but no azoxytoluene. (8') * *m*-Tolylhydroxylamine (32 grams), methyl alcohol (300 c.c.), and sulphuric acid (5 c.c.), after three months in the dark, gave 6-methoxy-*m*-toluidine (more than 10 grams), 5-amino-*o*-cresol (small amount), and azoxytoluene. (8'*a*) * *m*-Tolylazide (8 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and three hours' subsequent heating, gave 6-methoxy-*m*-toluidine (more than 1·7 grams), 5-amino-*o*-cresol (2·6 grams), and a trace of a phenolic substance, but no azoxytoluene. (9) * *p*-Xylylhydroxylamine (3·8 grams) and dilute sulphuric acid (1 : 10 by volume), after boiling for thirty-five minutes, gave 2-amino-*p*-5-xylenol (2 grams), *p*-xyloquinol (1·1 grams), and a small amount of azoxy-*p*-xylene. (9*a*) * *p*-Xylylazide (10 grams) and dilute sulphuric acid (1 : 3 by volume), after boiling for fifteen hours, gave 2-amino-*p*-5-xylenol (4·1 grams), *p*-xyloquinol (2·1 grams), but no azoxybenzene. (10)* *p*-Xylylhydroxylamine (5 grams), ethyl alcohol (175 c.c. of 96%), and sulphuric acid (2·5 c.c.), after three days at ordinary temperatures, gave 2-ethoxy-*p*-5-xylidine (1 gram) and azoxy-*p*-xylene (1·5 grams). (10*a*) * *p*-Xylylazide (15 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and two hours' gentle heating, gave 2-amino-*p*-5-xylenol (5·2 grams), 2-ethoxy-*p*-5-xylidine (4·6 grams), 2-ethoxy-*p*-5-xylenol (0·5 gram), and *p*-xyloquinol, but no azoxybenzene. (10') * *p*-Xylylhydroxylamine (11·1 grams), methyl alcohol (222 c.c.), and sulphuric acid (5·5 c.c.), after three weeks at room temperature, gave 2-methoxy-*p*-5-xylidine (theoretical amount) and traces of azoxy-*p*-xylene and *p*-xylidine. (10'*a*) * *p*-Xylylazide (5 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and four hours' heating, gave 2-methoxy-*p*-5-xylidine (2·5 grams), 2-amino-*p*-5-xylenol, but no azoxyxylene. (11) * *p*-Chlorophenylhydroxylamine (10 grams) and dilute sulphuric acid (1 : 5 by volume), after twenty-five minutes at 40—50°, gave *p*-chloroaniline (1·2 grams), *op*-dichloroaniline (0·45 gram), -*pp'*-dichloroazoxybenzene (5 grams), and traces of aniline. (11*a*) * *p*-Chlorophenylazide (10 grams) and dilute sulphuric acid (1 : 5 by volume), boiled for fifteen hours, gave *p*-chloroaniline (0·9 gram), *op*-dichloroaniline (0·45 gram), and traces of aniline, but no dichloroazoxybenzene. (12) (Cf. following abstract.) *p*-Chlorophenylhydroxylamine (5·5 grams) and dilute sulphuric acid (1 : 3), after heating for twenty minutes at 50°, gave *op*-dichloroaniline (2·4 grams), *p*-chloroaniline (0·7 gram), and *pp'*-dichloroazoxybenzene (1·5 grams). (12*a*) * *p*-Chlorophenylazide (5 grams) and dilute hydrochloric acid (20 grams concentrated acid and 40 grams of water), on boiling for twenty-two hours, gave *op*-dichloroaniline (1·8 grams), *p*-chloroaniline (0·45

gram), but no azoxybenzene derivative. (13)* *p*-Bromophenylhydroxylamine (10 grams) and dilute sulphuric acid (1 : 5), heated for fifteen minutes at 40—50°, gave *op*-dibromoaniline (0·3 gram), *p*-bromoaniline (2·4 grams), 5-bromo-*o*-aminophenol (small quantity), and *pp'*-dibromoazoxybenzene (5 grams). (13*a*) * *p*-Bromophenylazide (3 grams) and dilute sulphuric acid (1 : 5), on heating for fifteen hours, gave *op*-dibromoaniline, *p*-bromoaniline, a trace of 5-bromo-*o*-aminophenol, but no azoxybenzene derivative. (14) (Cf. A., 1912, i, 691.) *p*-Tolylhydroxylamine (14·5 grams) and dilute sulphuric acid (1 : 10 by volume), heated for forty minutes on the water-bath, gave toluquinol (9 grams), *p*-toluidine (2 grams), azoxy-*p*-toluene (0·9 gram), a small amount of *p*-cresol, and traces of 5-amino-*o*-cresol formed, probably, through the migration of the methyl group from the imino-ψ-quinol ether intermediately formed (a better instance of this change is discussed below). (14*a*) * *p*-Tolylazide (5 grams) and dilute sulphuric acid (1 : 3 by volume), after two hours' boiling, gave toluquinol (1 gram), *p*-toluidine (0·4 gram), and an odour of cresol, but no azoxytoluene or 5-amino-*o*-cresol. (14') *p*-Tolylhydroxylamine (30 grams) and dilute sulphuric acid (1 : 20 by volume), after fourteen hours' keeping at 18°, gave 11—12 grams of ψ-toluquinol (cf. A., 1912, i, 691). (14'*a*) * *p*-Tolylazide (22 grams) and sulphuric acid (1 : 1·75 water, by volume), after eleven hours' heating at 50—70°, gave ψ-toluquinol (0·6 gram), *p*-toluidine (5·4 grams), toluquinol (1 gram), *p*-cresol (0·1 gram), and traces of 5-amino-*o*-cresol, but no azoxy-derivative. (15) *p*-Tolylhydroxylamine and sulphuric acid gave "benzyleneimide" and its hydrate (*ibid.*). (15*a*) * *p*-Tolylazide and sulphuric acid gave "benzyleneimide" and its hydrate. (16) *p*-Tolylhydroxylamine, *p*-nitrotoluene, and sulphuric acid gave 2-nitro-4'-amino-5-methyldiphenylmethane (*ibid.*). (16*a*) * *p*-Tolylazide and sulphuric acid, after twenty-four hours at ordinary temperatures, yielded the same substance. (17) *p*-Tolylhydroxylamine (4·95 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), on heating for twenty minutes, gave *p*-hydroxyphenyl-*p*-tolylamine (3·4 grams) and doubtful traces of toluquinol and azoxytoluene (*loc. cit.*). (17*a*) * *p*-Tolylazide (6 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), on heating for two hours, gave *p*-hydroxyphenyl-*p*-tolylamine (about 4 grams), toluquinol (0·3 gram), and some *p*-toluidine. (18) * *p*-Tolylhydroxylamine (120 grams), methyl alcohol (1200 c.c.), and concentrated (100%) sulphuric acid (30 c.c.), after keeping for twenty-four hours at 10—20°, gave ψ-toluquinol 1-methyl ether (6·2 grams), *p*-toluidine (3 grams), and azoxy-*p*-toluene (65 grams). (18*a*) * *p*-Tolylazide (73·5 grams), methyl alcohol (230 c.c.), and concentrated sulphuric acid (100%) (100 c.c.), after ten hours at 13—22° and two days at 25—30°, gave ψ-toluquinol 1-methyl ether (2·5 grams), *p*-toluidine (0·85 gram), but no azoxytoluene. (18') * *p*-Tolylhydroxylamine (150 grams), ethyl alcohol (1250 c.c.), and 100% sulphuric acid (35 grams), after fifteen hours at room temperature, gave ψ-toluquinol-1-ethyl ether (10·9 grams), *p*-toluidine (11·9 grams), and azoxy-*p*-toluene (78 grams). (18'*a*) * *p*-Tolylazide (120 grams), ethyl

alcohol (370 c.c.), and 100% sulphuric acid (170 c.c.), after ten hours at 10—20° and a further 40 hours at 25—30°, gave ψ-toluquinol 1-ethyl ether (4 grams), *p*-toluidine (2·2 grams), but no azoxytoluene. (19) *m*-4-Xylylhydroxylamine (10 grams) and dilute sulphuric acid (1 : 10 by volume), on heating for twenty minutes on the water-bath, gave (A., 1912, i, 691) *p*-xyloquinol (4 grams), *m*-4-xylidine (1 gram), and traces of 2-amino-*p*-5-xylenol. (19*a*) * *m*-4-Xylylazide (60 grams) and dilute sulphuric acid (1 : 3 by volume), after six hours' heating, gave *m*-xyloquinol (0·4 gram), 2-amino-*p*-5-xylenol (1·1 grams), *m*-4-xylidine, and an odour of xylenol, but no azoxyxylene. The production of the *p*-xylene derivative (2-amino-*p*-5-xylenol) must be due to the migration of a radicle from the intermediate quinonoid products, for such an isomeric change is clearly necessary to enable them to pass into their benzenoid form. For example :

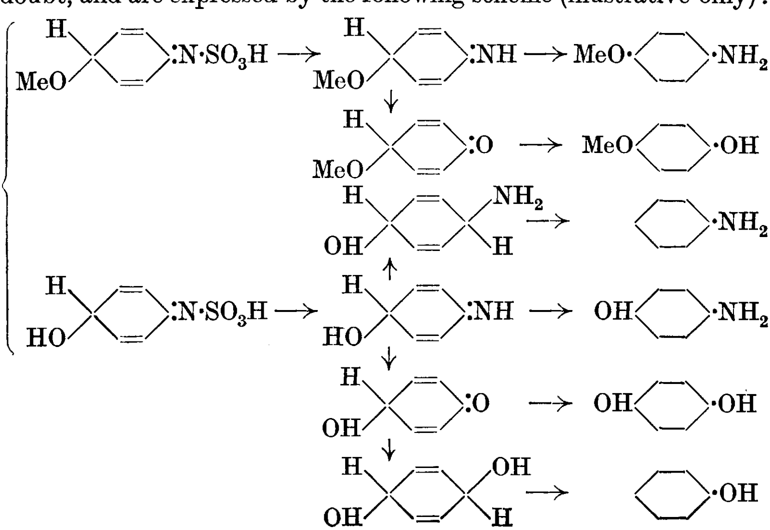


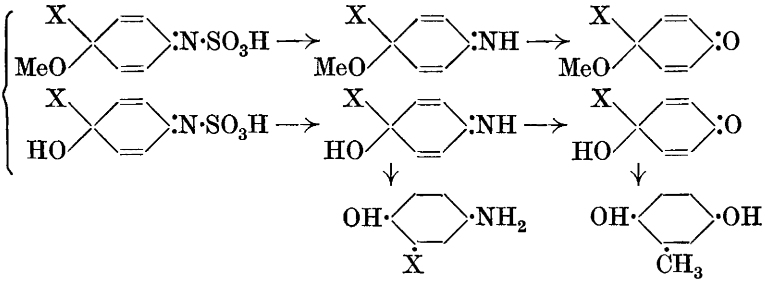
A similar mechanism is probably to be ascribed to the other cases of this kind mentioned in this paragraph. (19′) *m*-4-Xylylhydroxylamine (35 grams) and dilute sulphuric acid (17·5 grams H_2SO_4+350 c.c. of water), after eight to ten days' keeping at 23—25°, gave (cf. A., 1907, i, 516—520) ψ-*m*-xyloquinol monohydrate (22 grams), *m*-4-xylidine (6 grams), azoxyxylene (2·5 grams), and traces of 2-amino-*p*-5-xylenol. (19′*a*) * *m*-4-Xylylazide (10 grams) and dilute sulphuric acid (1 : 2 by volume), after eleven hours at 65°, gave ψ-*m*-xyloquinol (1·2 grams), *m*-4-xylidine (0·7 gram), and *p*-xyloquinol (0·3 gram) besides an odour of xylenol and some amorphous acids and bases. (20) (Cf. *loc cit.*) *m*-4-Xylylhydroxylamine (100 grams), ethyl alcohol (900 c.c.), and sulphuric acid (30 c.c.), after three hours' heating on the water-bath, gave ψ-*m*-xyloquinol ethyl ether (30 grams), 4 : 6-diethoxy-*m*-xylene (7 grams), 6-ethoxy-*m*-4-xylenol (0·15 gram), *m*-4-xylenol (0·2 gram), *p*-xyloquinol (trace), azoxy-*m*-xylene (5 grams), and *m*-xylidine (odour only). (20*a*) * *m*-4-Xylylazide (200 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after keeping at room temperature and then at 30—35°, gave ψ-*m*-xyloquinol ethyl ether (14·9 grams), 1 : 3-dimethylquinol (11·2 grams), *m*-4-xylenol (5 grams), *p*-xyloquinol (3·2 grams), *m*-4-xylidine (8 grams), and 2 : 5-diethoxy-*p*-xylene, but no azoxyxylene. (20′*a*) * *m*-4-Xylylazide (110 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume, 99·9%), after keeping at 12—17° and afterwards at 20—25°, gave 4-imino-ψ-*m*-xyloquinol 1-methyl ether (11 grams), 1 : 3-dimethylquinol methyl ether (27 grams), ψ-*m*-xyloquinol (1·4 grams), and *m*-4-xylidine, but no azoxyxylene. (20″*a*) * *m*-4-Xylylazide (140 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume, 100%), after keeping for eighteen hours at 20°, gave 4-imino-ψ-*m*-xyloquinol 1-ethyl ether (9·2 grams), ψ-*m*-xyloquinol methyl ether (14 grams), ψ-*m*-xyloquinol (1·5 grams), *p*-xyloquinol (0·07 gram),

2 : 5-diethoxy-*p*-xylene (0·35 gram), *m*-4-xylidine (3·1 grams), but no azoxyxylene. (21) (Cf. following abstract.) *m*-4-Xylylhydroxylamine (85 grams) and concentrated hydrochloric acid (saturated at 0°), after keeping for two weeks at 0° gave 5-chloro-*m*-4-xylidine (32 grams), 6-chloro-*m*-4-xylidine (29 grams), and azoxy-*m*-xylene (7 grams). (21*a*) * *m*-4-Xylylazide (12 grams) and concentrated hydrochloric acid (saturated at 0°), after keeping for four weeks, gave 5-chloro-*m*-4-xylidine (4·1 grams) and 6-chloro-*m*-4-xylidine (6·4 grams), but no azoxyxylene. (21′) (Cf. following abstract.) *m*-4-Xylylhydroxylamine (80 grams) and concentrated hydrobromic acid (saturated at 0°), after seven weeks in the dark, gave 5-bromo-*m*-4-xylidine (45 grams), 6-bromo-*m*-4-xylidine (0·07 gram), *m*-4-xylidine (7·5 grams), and azoxy-*m*-xylene (8·2 grams). (21′*a*) * *m*-4-Xylylazide (20 grams) and concentrated hydrobromic acid (saturated at 0°), after two days' keeping, gave 5-bromo-*m*-4-xylidine (17·2 grams), 6-bromo-*m*-4-xylidine (traces), *m*-4-xylidine (1·2 grams), but no azoxyxylene.

An examination of these facts reveals one striking qualitative difference. The production of azoxybenzene derivatives, which is almost always noticed in the transformation of the hydroxylamines, and in some instances occurs to a considerable degree, is never observed in the products of the reactions of the azides. For this reason, the suggestion made by Friedländer and Zeitlin (*loc. cit.*) that their observation of the formation of *o*-nitro-*p*-tolylhydroxylamine from *o*-nitro-*p*-tolylazide by the action of dilute acids is an indication of the general course pursued by the decomposition of the azides, is considered to be extremely improbable.

Apart from the formation of the azoxy-derivatives, there is clearly a close parallelism between the two sets of reactions, from which it is legitimate to argue that a similar mechanism must underlie the two cases. The later stages of the various processes can scarcely be in doubt, and are expressed by the following scheme (illustrative only):





This scheme holds both for hydroxylamines and azides, and the starting points are the quinonoid substances formed by the addition of water, sulphuric acid, methylsulphuric acid, etc., to the arylimide, Ar·N<. No plausible alternative is possible in the cases of the azides, and as on the evidence it is considered that a similar mechanism holds throughout for the azides and hydroxylamines, the latter also must be regarded as being initially broken down into arylimides and water.

In the cases of the hydroxylamines there is, superimposed, the known decomposition into azoxy-compounds and amines.

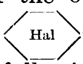
Although the evidence is strong, it is admitted that no arguments based on the character of the ultimate products can constitute an absolute proof (or disproof) of the mechanism suggested. C. K. I.

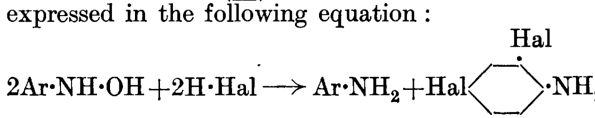
The Behaviour of Arylhydroxylamines towards the Hydrogen Haloid Acids. EUGEN BAMBERGER (*Annalen*, 1921, **424**, 297—321; cf. preceding abstract).—A large amount of experimental material on the subject is recorded and then submitted to a critical examination in order to unravel the various types of reaction occurring simultaneously.

The facts are the following: (1) Phenylhydroxylamine (2 grams) with dilute hydrochloric acid gave *p*-chloroaniline (1·6 grams), azoxybenzene (0·2 gram), a trace of *p*-aminophenol, and probably aniline. For the action of concentrated hydrochloric acid, see preceding abstract. (2) Phenylhydroxylamine with dilute hydrobromic acid gave *p*-bromoaniline (38%), some azoxybenzene, a trace of *p*-aminophenol, and probably some aniline. With concentrated acid, 60 grams of the hydroxylamine gave *p*-bromoaniline (22 grams), *o*-bromoaniline (5·3 grams), *op*-dibromoaniline (2·5 grams), and aniline (4 grams), but no azoxybenzene or aminophenol. (3) Phenylhydroxylamine (3 grams) and dilute hydriodic acid gave azoxybenzene (1·2 grams), aniline (0·6 gram), traces of *p*-aminophenol, and a blue dye. Concentrated acid gave aniline (more than 2 grams from 5) and a blue dye, but no azoxybenzene or aminophenol. (4) Phenylhydroxylamine (4 grams) and saturated hydrofluoric acid, after three weeks' keeping at 0°, gave azoxybenzene (0·1 gram), a volatile base thought to be *p*-fluoroaniline, and an amorphous substance containing fluorine. (5) For the action of concentrated hydrochloric acid on *o*-tolylhydroxylamine, see preceding abstract. Using concentrated hydrobromic acid,

26 grams of the hydroxylamine gave 5-bromo-*o*-toluidide (more than 10 grams), 3 : 5-dibromo-*o*-toluidine (4·3 grams), *o*-toluidine (more than 0·1 gram), azoxytoluene (1·3 grams crude), and doubtful traces of 6-amino-*m*-cresol. (6) *m*-Tolylhydroxylamine (3 grams) and dilute hydrochloric acid (10 parts of concentrated acid with 40 of water) gave 6-chloro-*m*-toluidine (0·6 gram), azoxy-*m*-toluene (0·5 gram), 5-amino-*o*-cresol (0·8 gram), a violet dye, and some gum. Dilute hydrobromic acid gave (from 3·4 grams of the hydroxylamine) 6-bromo-*m*-toluidine (0·8 gram), 5-amino-*o*-cresol (0·3 gram), and azoxy-*m*-toluene, a violet dye, and some gum. Saturated hydrobromic acid gave (from 4·5 grams of the hydroxylamine) 6-bromo-*m*-toluidine (2·5 grams), and a little azoxy-*m*-toluene. (7) *p*-Tolylhydroxylamine and dilute hydrochloric acid gave much *m*-chloro-*p*-toluidine, some *p*-toluidine, *m*-chloro-*p*-cresol, *p*-azoxytoluene, qualitative traces of *p*-nitrosotoluene, and possibly other products. (8) For the action of hydrochloric and hydrobromic acids on *m*-4-xylylhydroxylamine, see preceding abstract. (9) *p*-Xylylhydroxylamine (13 grams) and concentrated hydrochloric acid gave 5-chloro-*p*-2-xylidine (9·5 grams), 3 : 5-dichloro-*p*-2-xylidine (traces), and *p*-xylidine (traces). Saturated hydrobromic acid gave (from 11·2 grams of the hydroxylamine), 5-bromo-*p*-2-xylidine (11—12 grams), 3 : 5-dibromo-*p*-2-xylidine (1—1·5 grams), *p*-xylidine (0·5 gram), and some gum. (10) p-*Chlorophenylhydroxylamine*, m. p. 182° (very approximately), (5·5 grams), and dilute hydrochloric acid gave *op*-dichloroaniline (2·4 grams), *p*-chloroaniline (0·7 gram), *pp'*-dichloroazoxybenzene (1·5 grams), traces of aniline, qualitative traces of *o*-aminophenols and (doubtful) *s*-trichloroaniline. Fuming hydrochloric acid gave (from 7 grams of the hydroxylamine), *op*-dichloroaniline (4 grams), *s*-trichloroaniline (0·45 gram), *p*-chloroaniline (0·8 gram), *pp'*-dichloroazoxybenzene (0·25 gram), a little aniline, and gum. Dry hydrogen chloride in benzene solution gave (from 3·5 grams of the hydroxylamine) *op*-dichloroaniline (1·25 grams), *p*-chloroaniline (0·5 gram), *s*-trichloroaniline (trace), *pp'*-dichloroazoxybenzene, and qualitative traces of *o*-aminophenols. Dilute hydrobromic acid gave (from 5 grams of the hydroxylamine) *p*-chloro-*o*-bromoaniline, *p*-chloroaniline (0·9 gram), a little aniline, and *pp'*-dichloroazoxybenzene (1·6 grams); also qualitative traces of *o*-aminophenols. Saturated hydrobromic acid gave (from 12 grams of the hydroxylamine) *p*-chloro-*o*-bromoaniline (7 grams), *p*-chloro-*oo*-dibromoaniline (3·4 grams), *p*-chloroaniline (2 grams), *pp'*-dichloroazoxybenzene (0·3 gram), and qualitative traces of aniline and of *o*-aminophenols. (11) *p*-Bromophenylhydroxylamine (3 grams) with dilute hydrochloric acid gave *o*-chloro-*p*-bromoaniline (1·3 grams), *p*-bromoaniline (0·3 gram), *pp'*-dibromoazoxybenzene (0·7 gram), and qualitative traces of *o*-aminophenols. Concentrated hydrochloric acid gave (from 11 grams of the hydroxylamine) *o*-chloro-*p*-bromoaniline (5·7 grams), *s*-dichlorobromoaniline (1·9 grams), *p*-bromoaniline (1·7 grams), *pp'*-dibromoazoxybenzene, and qualitative traces of aniline and of *o*-aminophenols. Dilute hydrobromic acid gave (from 6 grams of the hydroxylamine) *op*-dibromoaniline (1·9

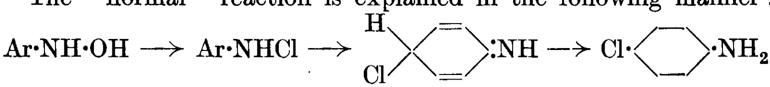
grams), *p*-bromoaniline (1 gram), *pp'*-dibromoazoxybenzene (2·3 grams), and an odour of *p*-bromonitrosobenzene (compare 7 above). Concentrated hydrobromic acid gave (from 11 grams of the hydroxylamine) *op*-dibromoaniline (5·7 grams), *s*-tribromoaniline (2·5 grams), and *p*-bromoaniline, besides traces of aniline and of *o*-aminophenols. (12) p-*Bromophenylhydroxylamine* (E. Feilmann, *Diss.*, Basle, 1898) (m. p. 66·5°) gave with dilute hydrochloric acid p-*chloro*-m-*bromoaniline* (m. p. 79·5—80°), an oily chlorobromoaniline (*acetyl* derivative, m. p. 117—118°), *mm'*-dibromoazoxybenzene, a doubtful trace of *o*-bromo-*p*-aminophenol, some dye, and much gum. With dilute hydrobromic acid the products were a *dibromoaniline* (m. p. 53°), *mm'*-dibromoazoxybenzene (50%), dye, and a trace of *p*-aminophenols.

Therefore, four chief types of reaction proceed simultaneously. In the first place, there is what may be termed the "normal" reaction, whereby a single halogen atom enters the ring, in the para-position if possible, in the ortho-position to some extent and particularly if the para-position is occupied, or in the meta-position, if, for instance, most of the other usual positions are occupied: Ar·NH·OH+H·Hal → ·NH_2. The second type of reaction is that expressed in the following equation:



This is termed the "abnormal" reaction. In addition, the hydroxylamines decompose into azoxy-compounds and amines, or by atmospheric oxidation into azoxy-compounds, or again by reduction (for example, by means of hydriodic acid) into amines. Finally, there is the type of decomposition due to the action of hydrogen ions and dealt with in the preceding abstract.

The "normal" reaction is explained in the following manner:



or by a similar mechanism involving an *o*-quinonoid intermediate product. The production of derivatives of *m*-chloroaniline is then easily explained by assuming addition of the halogen hydride to one of the double bonds of the quinonoid structure. The abnormal reaction also is discussed in the light of cognate reactions, but no entirely satisfactory solution is arrived at. C. K. I.

The Complete and Partial Reduction of Nitro-compounds with Iron. H. Pomeranz (*Chem. Zeit.*, 1921, **45**, 866—867).—When picric acid is reduced with iron and a large excess of hydrochloric acid in a similar manner to that used for 2 : 4-dinitrophenol (D.R.-P. 269542, A., 1914, i, 948) a blue-black powder is obtained as a result of the oxidation of triaminophenol. In this instance, the excess of hydrochloric acid does not protect the triamine owing to the rapid oxidation of ferrous chloride by unreduced picric acid.

On the other hand, picramic acid is neatly reduced to triaminophenol by this process. Picramic acid is usually prepared by reducing picric acid with sodium sulphide, but it may be obtained more cheaply by the use of iron and sulphurous acid (D.R.-P. 289454, A., 1916, i, 382). Picric acid is only slightly soluble in water, but when heated with water and iron it dissolves, probably as an iron salt. The prolonged passage of sulphur dioxide through such a solution results in rise of temperature and picramic acid separates. The yield is practically theoretical and the product is sufficiently pure for technical purposes. F. M. R.

Electrolytic Reactions of Naphthalene and its Derivatives. II. Electrolytic Oxidation of α-Naphthol. KASHICHI ONO (*J. Chem. Soc. Japan*, 1921, **42**, 559—578; cf. this vol., i, 334).—By the electrolytic oxidation of α-naphthol in acid solution, α-naphthaquinone, a compound of α-naphthol and α-naphthaquinone (*Ber.*, 1909, **42**, 1153), phthalic acid, and a dark violet compound are obtained in the anode chamber, whilst a red compound is produced in the cathode chamber. The dark violet compound, having a phenolic hydroxyl group, gave phthalic and phthalonic acids by oxidising with potassium permanganate, phthalic acid by fusing with potassium hydroxide, and naphthalene and αα-dinaphthol by distilling with zinc dust. The author gives optimum conditions for the operation. The electrolytic oxidation of αα-dinaphthol and α-naphthol-α-naphthaquinone to α-naphthaquinone, and to α-naphthaquinone and phthalic acid respectively, is described (cf. *J. Soc. Chem. Ind.*, 1921, Oct.). K. K.

Allyl Derivatives of Resorcinol and Quinol. F. MAUTHNER (*J. pr. Chem.*, 1921, **102**, 41—44).—The preparation and intramolecular transformation of allyl derivatives of phenols have been described by Claisen (A., 1913, i, 1175; 1919, i, 266) and the reactions have been used by the author (A., 1917, i, 544, and following abstract) in his investigations of plant substances. The behaviour of monomethylresorcinol and monomethylquinol has now been investigated.

Monomethylresorcinol dissolved in acetone is converted by allyl bromide in the presence of powdered potassium carbonate into 2-*methoxyphenyl allyl ether*, a colourless liquid, b. p. 125—126°/15 mm., which is transformed when heated with dimethylaniline into 2-*hydroxy*-4-*methoxyallylbenzene*, b. p. 143—144°/15 mm. The constitution of the latter substance is deduced from its complete methylation to 2 : 4-*dimethoxyallylbenzene*, a colourless liquid, b. p. 125—126°/14 mm., which is oxidised by potassium permanganate to dimethyl-β-resorcylic acid, m. p. 108°. 4-*Methoxyphenyl allyl ether*, b. p. 119—120°/13 mm., is transformed in the presence of boiling dimethylaniline into 6-*hydroxy*-3-*methoxyallylbenzene*, a colourless liquid, b. p. 144—145°/13 mm., which is converted by methyl sulphate into 3 : 6-dimethoxyallylbenzene, a colourless liquid, b. p. 126°/14 mm. H. W.

Synthesis of Pikamar. F. MAUTHNER (*J. pr. Chem.*, 1921, 102, 36—40).—Pikamar was isolated in 1833 by Reichenbach

from beechwood tar and examined subsequently by Hofmann (A., 1880, 248), Niederrist (*Monatsh.*, 1883, **4**, 487), and Will (A., 1888, 1089). The work of these chemists has sufficed to elucidate the constitution of the substance, but has not shown whether a propyl or an *iso*propyl group is present. The author has therefore synthesised 4-hydroxy-3 : 5-dimethoxy-*n*-propylbenzene, which is shown to be identical with pikamar.

2 : 6-Dimethoxyphenyl allyl ether (Mauthner, A., 1918, i, 428) is converted by being heated with dimethylaniline (compare Claisen, A., 1913, i, 1175) into 4-hydroxy-3 : 5-dimethoxyallylbenzene, which is transformed by acetyl chloride and glacial acetic acid into 4-*acetoxy*-3 : 5-*dimethoxyallylbenzene*, m. p. 43—44°. The latter is reduced by hydrogen in the presence of colloidal palladium to 4-acetoxy-3 : 5-dimethoxypropylbenzene, m. p. 87° (cf. Hofmann, *loc. cit.*), which, when hydrolysed, gives 4-hydroxy-3 : 5-dimethoxy-*n*-propylbenzene, b. p. 285°. H. W.

Synthesis and Dehydration of Phenylethylpropylcarbinol [γ-Phenylhexan-γ-ol]. VARTKÈS YÉRAMIAN (*Compt. rend.*, 1921, **173**, 362—364).—Propyl phenyl ketone reacts readily with magnesium ethyl bromide to give *γ-phenylhexan-γ-ol*, b. p. 132°/25 mm., which, when dehydrated by passing its vapour over infusorial earth at a red heat, gives *γ-phenyl-Δ^{γ}-hexene*, b. p. 216°. W. G.

Esters of Aminobenzoic Acids. HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1921, **43**, 1320—1323).—Certain esters of the aminobenzoic acids have been prepared by reduction of the corresponding nitrobenzoic esters, with the view of studying their anæsthetic properties. The following compounds are described. *Allyl* p-*nitrobenzoate*, a liquid, allyl *p*-aminobenzoate, m. p. 52°, giving a *hydrochloride*, m. p. 180°; iso*propyl* p-*nitrobenzoate*, m. p. 95°, iso*propyl* p-*aminobenzoate*, m. p. 79°, and its *hydrochloride*, m. p. 184°; n-*butyl* p-*nitrobenzoate*, m. p. 35°, *n*-butyl *p*-aminobenzoate, m. p. 58°, and its *hydrochloride*, m. p. 198°; n-*butyl* m-*nitrobenzoate*, liquid, n-*butyl* m-*aminobenzoate*, and its *hydrochloride*, m. p. 128°; n-*butyl* o-*aminobenzoate*, a liquid, and its *hydrochloride*, m. p. 178°; *ethyl* 3 : 5-*dinitrobenzoate*, m. p. 91°; ethyl 3 : 5-diaminobenzoate, m. p. 84°, and its *hydrochloride*, m. p. 248°; n-*butyl* 2 : 4-*dinitrobenzoate*, m. p. 70°, n-*butyl* 2 : 4-*diaminobenzoate*, m. p. 90°, and its *hydrochloride*, m. p. 270°; n-*butyl* 3 : 5-*dinitrobenzoate*, m. p. 61°, n-*butyl* 3 : 5-*diaminobenzoate*, and its *hydrochloride*, m. p. 253°.

A rough test of anæsthetic properties showed that *n*-butyl, allyl, and *iso*propyl *p*-aminobenzoates and *n*-butyl 3 : 5-diaminobenzoate were the most active and *n*-butyl 2 : 4-diaminobenzoate the least active as local anæsthetics. W. G.

The o-Diethylamino*cyclo*hexanylester of *p*-Aminobenzoic Acid. A. E. OSTERBERG and E. C. KENDALL (*J. Amer. Chem. Soc.*, 1921, **43**, 1370—1371).—*o*-Chloro*cyclo*hexanol reacts with diethylamine to yield o-*diethylamino*cyclo*hexanol*, b. p. 224°/730 mm., giving a *hydrochloride*, m. p. 160°. The alcohol condenses with

p-nitrobenzoyl chloride to give o-*diethylamino*cyclo*hexanyl* p-*nitrobenzoate*, giving a *hydrochloride*, m. p. 175°, which on reduction with tin and hydrochloric acid gives o-*diethylamino*cyclo*hexanyl* p-*aminobenzoate*, m. p. 72°, and its *hydrochloride*, m. p. 163°. The physiological action of this ester is being studied. W. G.

Condensation of Nitriles and Thioamides. I. Benzonitrile and Thiobenzamide. SEIICHI ISHIKAWA (*J. Chem. Soc. Japan*, 1921, **42**, 579—586).—Matsui (*Mem. Coll. Sci. Eng. Kyoto*, 1910, **2**, 401) isolated a condensation product of benzonitrile and thiobenzamide, and considered it to be benziminosulphide, $S(CPh{:}NH)_2$. The author oxidised the condensation product with $0{\cdot}1N$-iodine in alcoholic solution, and found that the quantity of iodine used, the nature of the resulting product, and the non-evolution of hydrogen sulphide do not support this view. By reducing the substance with zinc dust and hydrochloric acid in alcoholic solution, benzylbenzamidine was isolated, accompanied by the evolution of hydrogen sulphide, indicating the presence of the groups $-C({:}N){\cdot}N{\cdot}C-$ and $-SH$. Moreover, by alkylation with ethyl iodide, it gave ethyl benziminoisothiobenzamide hydriodide, yellow, monoclinic crystals, m. p. 181°, the ethyl group combining with the sulphur atom. The condensation would therefore appear to proceed as follows, producing benziminoisothiobenzamide: $SH{\cdot}CPh{:}NH + PhCN = SH{\cdot}CPh{:}N{\cdot}CPh{:}NH$. K. K.

The Nitro- and Amino-derivatives of *m*-Hydroxybenzoic Acid. VICTOR FROELICHER and JULIUS BEREND COHEN (T., 1921, **119**, 1425—1432).

The Additive Properties of the Keto-enolic Double Linking. H. GAULT and R. WEICK (*Compt. rend.*, 1921, **173**, 391—393).—Ethyl phenylpyruvate reacts with acid anhydrides and acid chlorides, giving the corresponding esters. Thus with acetic anhydride the β-ester gives *ethyl α-acetoxycinnamate*, $CHPh{:}C{<}^{CO_2Et}_{OAc}$, m. p. 33—34°, and with benzoyl chloride the corresponding *benzoyloxy*-derivative, m. p. 87°. These two derivatives do not form additive compounds with bromine, but always yield substituted compounds. The presence of the double linking is verified by the fact that they immediately decolorise potassium permanganate in alkaline solution. Dilute potassium hydroxide solution rapidly regenerates ethyl phenylpyruvate from these two derivatives. W. G.

Resolution of *dl-trans-cyclo*Pentane-1 : 3-dicarboxylic Acid. WILLIAM HENRY PERKIN, jun., and HAROLD ARCHIBALD SCARBOROUGH (T., 1921, **119**, 1400—1408).

The Dinaphthanthracene Series. IV. Bromo-derivatives. ERNST PHILIPPI and FEDORA AUSLAENDER (*Monatsh.*, 1921, **42**, 1—4; cf. A., 1911, i, 793; 1913, i, 627; 1914, i, 826; Mills and Mills, T., 1912, **101**, 2194).—Pyromellitic anhydride condenses with bromobenzene in the presence of aluminium chloride to yield a mixture of 2 : 5-*di*-p-*bromobenzoylterephthalic acid*, m. p. 306—

309° (decomp.) and 4 : 6-*di*-p-*bromobenzoyl*iso*phthalic acid*, m. p. 256—260° after previous decomposition, which are separated by crystallisation from glacial acetic acid; by analogy with the dibenzoylphthalic acids, the substance of higher melting point is considered to have the carboxyl groups in the para-position to one another. The acids lose water when heated with concentrated sulphuric acid, giving 2 : 9-*dibromo*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, greenish- or brownish-yellow needles, which gradually darken and decompose above 250°, and 2 : 10-*dibromo*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* respectively. H. W.

New Method for the Preparation of Mellitic Acid. Ernst Philippi and Gertrud Rie (*Monatsh.*, 1921, **42**, 5—8).—1 : 3 : 5-*Trimethyl*-2 : 4-*diethylbenzene*, a colourless liquid, b. p. 229—236°, is obtained by the reduction of diacetylmesitylene with amalgamated zinc and hydrochloric acid; it is converted by acetyl and aluminium chlorides in the presence of carbon disulphide into 6-*acetyl*-1 : 3 : 5-*trimethyl*-2 : 4-*diethylbenzene*, a pale yellow liquid with a powerful odour of violet root, b. p. 286—304°, which is reduced to 1 : 3 : 5-*trimethyl*-2 : 4 : 6-*triethylbenzene*, a colourless liquid, b. p. 238—247°. The acetyl compound is oxidised by nitric acid to mellitic acid, m. p. 285—286°. H. W.

Constitution of the Bile Acids. W. Borsche (*Nachr. Ges. Wiss. Göttingen*, 1920, 188—194; from *Chem Zentr.*, 1921, iii, 174. Cf. A., 1919, i, 276, 476).—[With Herbert Behr.]—*iso*-α-*Cholanetricarboxylic acid*, obtained by reduction of *iso*bilianic acid with zinc and hydrochloric acid in glacial acetic acid solution, gives colourless needles, m. p. 261° (decomp.). The *trimethyl* ester, $C_{27}H_{44}O_6$, forms lustrous leaflets, m. p. 103—104°.

[With Hans Wieckhorst.]—*Ethyl dihydrogen* β-*cholanonetricarboxylate*, $C_{26}H_{40}O_7$, gives long, white needles, m. p. 136°. The *monomethyl* ester has m. p. 247°. The *oxime*, $C_{24}H_{37}O_7N$, forms transparent crystals, m. p. 227°. By heating with 90% sulphuric acid an isomeric *oximic acid* is obtained by rearrangement, giving stout, lustrous crystals decomposing at 273—274°. β-*Cholanedionecarboxylic acid dioxime*, $C_{24}H_{38}O_4N_2$, sinters at 250° and decomposes at 273°. The iso*oxime* has m. p. 164°. The *acid* has m. p. 274—275°. It is prepared by the reduction of β-cholanetricarboxylic acid. By distillation of β-cholanetricarboxylic acid in a vacuum, a distillate is obtained from which, after repeated recrystallisation from acetic acid, a *substance* is obtained, m. p. 205—207°. From mono-ethyl β-cholanetricarboxylate, the *anhydride*, $C_{26}H_{38}O_6$, is obtained by distillation. G. W. R.

Preparation of Hydroxyaryl Aldehydes. Hermann Haakh (Brit. Pat. 157850).—Hydroxyaryl aldehydes are obtained by treating phenols with formaldehyde in presence of a nitroso-compound and an acid condensing agent. An azo-methine is formed intermediately, and decomposes into aldehyde and amine. For example, 60 grams of guaiacol and 109 grams of nitrosodiethylaniline hydrochloride (or the corresponding amount of nitrosophenol), dissolved in 500 grams of methyl alcohol, are saturated

with hydrogen chloride and boiled in a reflux apparatus. Seventy grams of 23% formaldehyde solution are slowly added, and when the reaction is complete the alcohol is distilled off. From the residue, after boiling for a short time in feebly alkaline solution followed by re-acidification, the vanillin is extracted with ether and purified in the usual way. G. F. M.

The Allyl*cyclo*hexanones and the Methylallyl*cyclo*hexanones. R. CORNUBERT (*Ann. Chim.*, 1921, [ix], **16**, 141—220).—A more detailed account of work already published (cf. A., 1914, i, 951, 969; 1920, i, 390, 485; this vol., i, 422; ii, 5). W. G.

Action of Nitroso-derivatives on Unsaturated Compounds. L. ALESSANDRI (*Gazzetta*, 1921, **51**, ii, 129—144).—A fuller account is given of work already published (A., 1915, i, 555).

The action of nitrosobenzene on estragole in the dark yields the *compound*, $C_{16}H_{15}O_2N$, which forms stellar aggregates of golden-yellow, prismatic needles, m. p. 165°. Nitrosobenzene and methyl-eugenol give the *compound*, $C_{17}H_{17}O_3N$, in stellar aggregates of highly refractive, yellow prisms, m. p. 154°, decomposing rapidly in direct sunlight, and nitrosobenzene and myristicin, the *compound*, $C_{17}H_{15}O_4N$, which forms groups of deep yellow scales, m. p. 180°, and is decomposed gradually by diffused, and rapidly in direct, sunlight.

In addition to the products named (*loc. cit.*), azoxybenzene is formed by the action of nitrosobenzene on parsley-apiole.

The action of nitrosobenzene on *iso*safrole does not give the N-phenyl derivative of piperonaldoxime, as would be expected from the course followed by the interaction of nitrosobenzene and asarone (*loc. cit.*), but is accompanied by secondary oxidation and reduction, piperonaldehyde being detectable among the products, together with a substance yielding aniline when boiled with dilute acid. T. H. P.

Unsaturated Compounds. III. Condensation of *p*-Aminoacetophenone and Acetyl-*p*-aminoacetophenone with Aromatic Aldehydes. M. GIUA and E. BAGIELLA (*Gazzetta*, 1921, **51**, ii, 116—125; cf. A., 1920, i, 676).—By the condensation of *p*-aminoacetophenone or its acetyl derivative with various aromatic aldehydes in alcoholic solution containing sodium or potassium hydroxide, unsaturated ketones have been obtained (cf. Scholtz and Huber, A., 1904, i, 253). These have been treated with bromine in order to ascertain if the presence in the aromatic ring of the group ·NHR influences in any particular way the manner in which the halogen is added to the double linking.

p-Benzylideneaminoacetophenone and the compound, m. p. 143°, prepared from *p*-aminoacetophenone and benzaldehyde in alcoholic solution containing sodium hydroxide, have been already described by Scholtz and Huber (*loc. cit.*). The action of bromine on the compound, m. p. 143°, yields: (1) a *compound*, $C_{22}H_{17}ONBr_4$, m. p. 145° (crude), and (2) a pale yellow, amorphous compound, m. p. 209°, containing 59·67% of bromine.

p-*Anisylideneaminoacetophenone*, $OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$,

forms silvery needles, m. p. 124—125°, and gives an intense orange-yellow coloration with concentrated sulphuric acid.

The *compound*, $OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$, crystallises in yellow lamellæ, m. p. 149—150°, and, like the compound, m. p. 191°, obtained by Scholtz and Huber from anisaldehyde and *p*-aminoacetophenone, forms a purple coloration with concentrated sulphuric acid. The action of bromine in chloroform solution on the compound, m. p. 149—150°, gives a pale orange, amorphous compound containing 43·98% of bromine, the latter replacing hydrogen atoms of the aromatic nuclei as well as saturating the double linking.

p-*Cinnamylideneaminoacetophenone*,

$$CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3,$$

forms lustrous, pale yellow plates, m. p. 126—127°.

The compound, $CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CHPh$, obtained from cinnamaldehyde and *p*-aminoacetophenone, forms golden-yellow needles, m. p. 162—163°, and gives a reddish-violet coloration with concentrated sulphuric acid. The compound, m. p. 191°, to which Scholtz and Huber ascribed this structure, is probably the result of more advanced condensation. The *hexabromide*, $CHPhBr{\cdot}CHBr{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}CHBr{\cdot}CHPhBr$, is a deep yellow, amorphous compound, m. p. 192° (decomp.).

Benzylidene-*p*-acetylaminoacetophenone, obtained from *p*-acetylaminoacetophenone and benzaldehyde, forms yellow crystals, m. p. 168°, and gives a reddish-yellow coloration with concentrated sulphuric acid; Rupe and Porai-Koschitz (A., 1906, i, 754) gave m. p. 179°. Its *dibromide*, $CHPhBr{\cdot}CHBr{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3$, crystallises in pale yellow prisms, m. p. 175°.

Anisylidene-p-*acetylaminoacetophenone*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_3,$$

crystallises in yellow lamellæ, m. p. 198°, and forms a red, oily, dibromide, which could not be purified.

Cinnamylidene-p-*acetylaminoacetophenone*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NHAc,$$

forms yellow crystals, m. p. 183—184°, reddens rapidly when left moist in the air, and gives a brick-red coloration with concentrated sulphuric acid. Its *tetrabromide*, $C_{19}H_{17}O_2NBr_4$, crystallises in white needles, m. p. 195° (decomp.).

In chloroform or benzene solution, cinnamylideneacetophenone is converted by the action of light into a dimeric modification which, when heated, undergoes transformation into the monomeride, *iso*cinnamylideneacetophenone (Stobbe and Rücker, A., 1911, i, 385). Attempts to prepare, in a similar way, the dimeride of cinnamylidene-*p*-acetylaminoacetophenone have proved unsuccessful. T. H. P.

The Influence of Steric Factors on Intramolecular Condensation. James Kenner and Ernest Witham (T., 1921, **119**, 1452—1461).

Crystalline Form of Trimethylphloretin. Maria De Angelis (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 348—351).—This com-

pound, $C_6H_2O_3Me_3{\cdot}CO{\cdot}CHMe{\cdot}C_6H_4{\cdot}OH$ (compare Ciamician and Silber, A., 1895, i, 538), forms crystals belonging to the prismatic class of the monoclinic system, $a:b:c=0{\cdot}4505:1:0{\cdot}3410$, $\beta=71^\circ\ 13'$; $d=1{\cdot}306$. T. H. P.

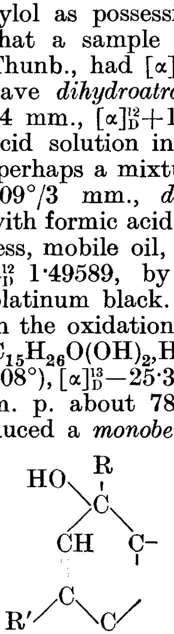
Migration of the Sulphonic Acid Group in Aromatic Molecules. JH. MARTINET (*Rev. gén. Mat. colorantes*, 1921, **25**, 49—51; from *Chem. Zentr.*, 1921, iii, 224—225).—The sulphonation of anthraquinone takes place first in the α-position and then in the β-position. The formation of the β-sulphonic acid is due to transformation from the α-acid. In the absence of other substances, the sulphonation of anthraquinone requires a fairly high temperature, and under such conditions the rate of transformation of the α- into the β-sulphonic acid is of the same order as the formation of the α-acid, with the result that only the β-acid is obtained. In order to obtain the α-acid, it is necessary to employ a catalyst which lowers the temperature of sulphonation without influencing the rate of transformation of the α- into the β-acid. By the use of mercury in this way as a catalyst, the α-sulphonic acid can be obtained at a lower temperature. That this explanation is correct was shown (in collaboration with A. Roux) by the fact that the α-sulphonic acid thus prepared is transformed into the β-acid at a higher temperature. The transformation also takes place even in the presence of mercury with suitable conditions of temperature and concentration. In order to obtain the 1 : 5-disulphonic acid, the reaction must take place at a higher temperature, and more sulphur trioxide must be used. G. W. R.

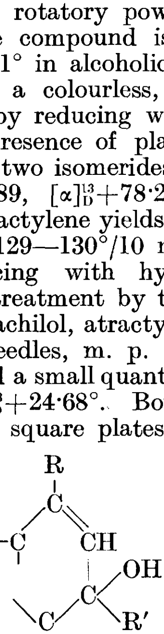
Some Derivatives of Anthraquinonedi-imide. LEON PIERRE GEORGE KEFFLER (T., 1921, **119**, 1476—1482).

Sesquiterpene Groups. II. Machilol and Atractylol. SEISI TAKAGI (*J. Pharm. Soc. Japan*, 1921, No. **473**, 565—587).—By distilling Formosan *Machilus Kusanoi*, Hayata (Lauraceæ), in steam, a light yellow, viscous oil was obtained. The fraction 140—170°/5 mm. was recrystallised from dilute alcohol and sublimed in a vacuum, yielding a new sesquiterpene alcohol, *machilol*, $C_{15}H_{26}O$, white needles, m. p. 79—80°, b. p. 160°/14 mm., $[\alpha]_D^{25}+30{\cdot}08^\circ$ in alcohol. The alcohol decolorises potassium permanganate and bromine solutions, but does not form an ester or phenylurethane. By reducing with hydrogen in the presence of platinum black in alcoholic solution, the alcohol gave *dihydromachilol*, $C_{15}H_{28}O$, m. p. 82—83°, b. p. 157—158°/14 mm., $[\alpha]_D^{18}+16{\cdot}43^\circ$, in alcohol. By heating with formic acid, machilol yields *machilene*, $C_{15}H_{24}$, a colourless oil, $d_4^{23}=0{\cdot}9109$, $[\alpha]_D^{23}+58{\cdot}73$, $n_D^{23}=1{\cdot}51257$, by losing one molecular proportion of water. The product is, however, apparently a mixture of two isomerides, since the specific rotation of the product is not constant, but varies according to the time and temperature of heating with formic acid. Machilene yields *tetrahydromachilene*, a colourless, mobile oil, b. p. 132°/11 mm., $d_4^{10}=0{\cdot}8964$, $[\alpha]_D^{10}+37{\cdot}04^\circ$, $n_D^{10}=1{\cdot}48645$, by reducing with hydrogen in glacial acetic acid solution, using platinum black as catalyst.

By oxidation with dilute potassium permanganate in benzene solution, machilol gave *dihydroxymachilol*, $C_{15}H_{26}O(OH)_2,H_2O$, white needles, m. p. 110° (*anhydride*, m. p. 107—108°), which gave a *monobenzoate*, white, square plates, m. p. 142°, by the Schotten-Baumann method.

Gadamer and Amenomiya (A., 1903, i, 353), described atractylol as possessing no rotatory power, whilst the author found that a sample of the compound isolated from *Atractylis ovata*, Thunb., had $[\alpha]_D^{13} -17{\cdot}1°$ in alcoholic solution. The same sample gave *dihydroatractylol*, a colourless, viscous oil, b. p. 156—158°/14 mm., $[\alpha]_D^{12} +14{\cdot}9°$, by reducing with hydrogen in glacial acetic acid solution in the presence of platinum black; and *atractylene* (perhaps a mixture of two isomerides), a colourless oil, b. p. 108—109°/3 mm., d_4^{13} 0·9189, $[\alpha]_D^{13} +78{\cdot}25°$, n_D^{13} 1·51795, by heating with formic acid. Atractylene yields *tetrahydroatractylene*, a colourless, mobile oil, b. p. 129—130°/10 mm., d_4^{11} 0·9030, $[\alpha]_D^{12} + 36{\cdot}99°$, n_D^{12} 1·49589, by reducing with hydrogen in the presence of platinum black. On treatment by the same method as was used in the oxidation of machilol, atractylol gave *α-dihydroxyatractylol*, $C_{15}H_{26}O(OH)_2,H_2O$, needles, m. p. 110° (*anhydride*, m. p. 107—108°), $[\alpha]_D^{13} -25{\cdot}34°$, and a small quantity of the β-isomeride, needles, m. p. about 78°, $[\alpha]_D^{13} +24{\cdot}68°$. Both α- and β-compounds produced a *monobenzoate*, square plates, m. p. 142°, by the Schotten-Baumann method. Thus dihydroxy- and tetrahydromachilol are identical with dihydroxy- and tetrahydroatractylol respectively. Machilol (annexed formula I) and atractylol (II) and the corresponding hydrocarbons have therefore the same constitutional skeleton, differing in the positions of the double bonds and the hydroxyl group. K. K.


(I.)


(II.)

Swelling of Caoutchouc in Various Liquids. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1921, **29**, 100—105).—A theoretical paper in which an attempt is made to establish a connexion between the swelling power of a substance and some definite physical property of the liquid which effects the swelling. The previously published results of Flusin (A., 1908, ii, 359) and Posnjak (A., 1912, ii, 912) on the swelling of caoutchouc in a series of liquids have been used. As a first approximation, it is shown that the swelling power decreases with increasing dielectric constant of the liquid. This is expressed by the equation $\sqrt[n]{Q}\,.\,D=K$, in which Q is the swelling power, D the dielectric constant, K a constant, and n a number between 2 and 3. If n is chosen as 2·16, the mean value of K for 14 solvents ($D=2{\cdot}3$—81) is 50, with extreme values of 74 and 29. These variations are regarded as accidental, and due in part to inexact values of the dielectric constant. It is shown that swelling power and solubility cannot be directly compared, but swelling

power and the reciprocal of the solubility (Lösungsmittelbedarf) may. The similarity of the above relationship to the Walden relationship between the solubility and the dielectric constant, $D=\sqrt[3]{\mu}\,.\,K$, is pointed out and discussed. J. F. S.

Mechanism of the Action of certain Accelerants of the Vulcanisation of Caoutchouc. G. BRUNI and E. ROMANI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 337—344).—It has been commonly assumed that accelerators of vulcanisation are substances capable of reacting with the added sulphur to form polysulphides, which then yield their sulphur with liberation of the original accelerating compounds. This hypothesis has been advanced in various forms by Ostromisslenski (A., 1916, i, 277), Kratz, Flower, and Coolidge (*J. Ind. Eng. Chem.*, 1920, **12**, 317), and Bedford and Scott (*J. Ind. Eng. Chem.*, 1920, **12**, 31). Most probably true is the view of the last of these authors, who distinguish between the two types of accelerators: (1) Bases forming polysulphides similar to yellow ammonium sulphide, and (2) thiocarbamides, dithiocarbamates, thiourams, mercaptans, and the disulphides formed from them by oxidation or by reaction with sulphur. To the latter group, which alone contains accelerators sufficiently active to be termed ultra-accelerators, must be added alkylxanthates (cf. this vol., i, 575).

Thiouram disulphides are obtainable by the oxidation of dithiocarbamates of imines or by subjecting metallic dithiocarbamates to oxidation or to the action of sulphur:

$$(NR_2{\cdot}CS{\cdot}S)_2Zn+S=ZnS+(NR_2{\cdot}CS{\cdot}S)_2,$$

and this equation represents the manner in which zinc alkyl- and aryl-dithiocarbamates act in the caoutchouc–sulphur mixture. Similarly, zinc alkylxanthates are able to function as ultra-acclerators, since they readily undergo oxidation to form disulphides, $(NR_2{\cdot}CS)_2S_2$, which are perfectly analogous to those of the thiourams, the so-called dixanthogens, $(OR{\cdot}CS)_2S_2$. It is thus definitely shown that the presence of nitrogen and the possession of basic properties are quite unnecessary in an accelerator.

Ultra-accelerating effects are exerted in presence of metallic oxides also by the thiolbenzthiazoles, for instance, $C_6H_4<^{N}_{S}>C{\cdot}SH$, and by the disulphides they yield on oxidation $\left(C_6H_4<^{N}_{S}>C\right)_2S_2$. Since thiolbenzthiazole may be obtained in good yield by the action of sulphur on methyleneaniline (anhydroformaldehyde-aniline), the cause of the accelerating action of the latter is evident.

Trisubstituted thiocarbamides are able to yield thiocarbimides, $NHAr{\cdot}CS{\cdot}NR_2 \longrightarrow NAr{:}C{:}S+NHR_2$, and thus act as accelerators in the same way as the above compounds. On the other hand, tetra-substituted thiocarbamides, which do not undergo this reaction, are totally devoid of accelerating properties.

The function of zinc oxide in favouring acceleration consists in the formation of the zinc salts of the thio-acids, these by the action of free sulphur losing the zinc as zinc sulphide and yielding the organic disulphides which are the true accelerators. T. H. P.

Sols and Gels of Vulcanised Caoutchouc. HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1921, **40**, 186T—190T).—Although vulcanised caoutchouc does not dissolve in the ordinary solvents, solutions of vulcanised caoutchouc can be obtained by heating solutions of raw caoutchouc with sulphur to the customary vulcanising temperatures. With xylene or toluene as solvent, combination of rubber with sulphur proceeds more rapidly than when benzene is used; with a 10% solution of a mixture of caoutchouc and sulphur (90 : 10) in this solvent, the rate of combination is about half that with the dry mixture at the same temperature. Vulcanisation of a dilute solution does not cause any great change in viscosity. Solutions of vulcanised caoutchouc prepared in this manner, on evaporation, yield films which refuse to redissolve in the solvent. If the solutions are too concentrated or if vulcanisation progresses too far, gelation occurs. Similar behaviour is observable in the vulcanisation of dissolved caoutchouc with sulphur chloride at the ordinary temperature. Vulcanisation in solution can also be effected, with the aid of heat, by trinitrobenzene in the presence of litharge. On exposure to light, the solutions of caoutchouc vulcanised with sulphur or sulphur chloride gelatinise, the effect being reversible in the dark; prolonged exposure to light may cause the primarily produced gels to liquefy owing to degradation of the caoutchouc. D. F. T.

Phenolcoumarein and Resorcinolcoumarein. SRI KRISHNA (T., 1921, **119**, 1420—1425).

Arylated Pyridines and their Relationships to the Corresponding Pyrylium Compounds. II. WALTHER DILTHEY [with G. BAURIEDEL, B. BURGER, G. GEISSELBRECHT, F. VON IBACH, F. KIEFER, A. SEEGER, O. SIMON, R. TAUCHER, and J. WINKLER] (*J. pr. Chem.*, 1921, **102**, 209—240; cf. A., 1920, i, 448).—Arylpyridines are readily accessible, since it has been found that purely aromatic pyrylium salts and their *pseudo*-bases, like the corresponding aliphatic derivatives (cf. Baeyer and Piccard, A., 1911, i, 901) are readily converted by ammonia into arylpyridines. The yields are quantitative when the pyrylium iron salt is decomposed in a medium in which the pyridine produced is soluble. With increases in the number of phenyl groups present in the molecule, the basicity of the phenylated pyridine diminishes, or, at any rate, the stability of the salts towards water becomes less. Simultaneously, the addition of methyl iodide becomes more difficult. This behaviour is in striking contrast with the existence of tetra- and penta-phenylated pyrylium salts and is regarded by the author as further confirmation of his formulation of pyrylium salts in which the acid radicle is regarded as attached to the whole of the remainder of the molecule instead of to a specific atom. A further point of contrast between pyrylium and pyridine compounds is afforded by the ready convertibility of the former into quinopyran derivatives, whereas the latter do not appear to be able to yield similar compounds. In accordance with the conceptions of Hantzsch (A., 1920, i, 34) the salts of the arylpyridines are regarded

as non-ionised additive compounds. Such as have been analysed contain acid and base in molecular proportions, but indications are not lacking that union can also occur with more than one molecular proportion of acid, the effect being hypsochromic.

The following individual compounds are described: 4-*phenyl*-2 : 6-*di*-p-*chlorophenylpyridine* (from a suspension of the 4-phenyl-2 : 6-di-*p*-chlorophenylpyrylium iron salt and ammonia), slender, colourless needles, m. p. 183° (*hydrochloride*, m. p. about 250°; *picrate*, lemon-yellow needles, m. p. 236°); 4 : 6-*diphenyl*-2-β-*naphthylpyridine*, almost colourless needles, m. p. 124—125° (*picrate*, yellow needles, m. p. 233—234°); 4-*phenyl*-2 : 6-*di*-p-*tolylpyridine*, almost colourless crystals, m. p. 158—159° (*hydrochloride, nitrate*; *picrate*, pale yellow needles, m. p. 222°); 2 : 4-*diphenyl*-6-p-*tolylpyridine*, almost colourless, lustrous leaflets, m. p. 121° (*hydrochloride*, indefinite m. p., *picrate*, pale yellow prisms, m. p. 192°); 4 : 6-*diphenyl*-2-p-*diphenylylpyridine*, almost colourless needles, m. p. 141° (*chloride*, decomp. about 130°; *picrate*, yellow prisms, m. p. 180°); 2 : 6-*diphenyl*-4-p-*anisylpyridine*, lustrous leaflets, m. p. 100—101° (*picrate*, yellow crystals, m. p. 192°; *chloride*; *bromide*); 2 : 6-*diphenyl*-4-p-*hydroxyphenylpyridine* (from the methoxy-compound and concentrated hydrochloric acid at 160°), slender, colourless needles, m. p. 214—215° (*picrate*, yellow crystals, m. p. 219—220°; *methiodide*, a relatively unstable substance, m. p. about 190°, which is converted by sodium picrate into the corresponding *picrate*, yellow needles, m. p. 210°); 2 : 6-*diphenyl*-4-p-*acetoxyphenylpyridine*, colourless crystals, m. p. 110—112° (*picrate*, yellow, silky needles, m. p. 170—171°); 4 : 6-*diphenyl*-2-p-*anisylpyridine*, m. p. 100—102° (*picrate*, m. p. 210°; *chloride*; *bromide*; very unstable *methiodide*); 4 : 6-*diphenyl*-2-p-*hydroxyphenylpyridine*, m. p. 189—190° (*chloride*, greenish-yellow needles; *picrate*, yellow crystals, m. p. 243—244°; *sodium* salt ($+4H_2O$), colourless, silvery leaflets, (anhydrous) lemon-yellow powder; *potassium* salt; *methiodide*, coarse, greenish-yellow crystals, m. p. 208—210°, and the corresponding *picrate*, yellow crystals, m. p. 194°); 4 : 6-*diphenyl*-2-p-*acetoxyphenylpyridine*, colourless needles, m. p. 113—114°; 6-*phenyl*-2 : 4-*di*-p-*anisylpyridine*, colourless crystals, m. p. 108—110° (*picrate*, lemon-yellow prisms, m. p. 174—176°; *bromide*, slender, colourless needles; *chloride*); 6-*phenyl*-2 : 4-*di*-p-*hydroxyphenylpyridine* (from the preceding compound and concentrated hydrochloric acid at 160—180°), almost colourless needles, m. p. 222° (*picrate*, lemon-yellow prisms, m. p. 245°; *bromide*, yellow needles; *chloride*; *di-acetyl* derivative, m. p. 140—141°, and its *picrate*, small, yellow needles, m. p. 172°; *dibenzoyl* derivative, colourless needles, m. p. 147—149°; *methiodide*, unstable, yellow crystals, m. p. 193—194° and the corresponding *picrate*, yellow needles, m. p. 198—200° after undergoing alteration at 134°); 4-*phenyl*-2 : 6-*di*-p-*anisylpyridine*, slender, silky needles, m. p. 133—134° (*picrate*, yellow needles, m. p. 193—194°; *chloride*, greenish-yellow needles, m. p. (indefinite) 138—155°; *bromide*, m. p. about 160° (indefinite); very unstable *methiodide*); 4-*phenyl*-2 : 6-*di*-p-*hydroxyphenylpyridine* (from the

methoxy-compound and hydrochloric acid), almost colourless silky needles, m. p. 228—229°, (*di-potassium* salt, colourless needles; *picrate*, m. p. 256°; *chloride*, yellow needles without definite melting point and the analogous *bromide*; *methiodide*, m. p. 228—229° decomp. and the corresponding *picrate*, orange-yellow crystals, m. p. 250—252°; *di-acetyl* derivative, colourless crystals, m. p. 147—148° and its *picrate*, yellow prisms, m. p. 157—159°; *dibenzoyl* compound, m. p. 206—207°); 2 : 4 : 6-*tri*-p-*anisylpyridine*, colourless, silky needles, m. p. 133° (*picrate*, yellow needles, m. p. 196°; *chloride*, m. p. above 150°; *bromide*, m. p. about 190°, indefinite; unstable *methiodide*, m. p. about 148°); 2 : 4 : 6-*tri*-p-*hydroxyphenylpyridine*, yellowish-white needles, m. p. 282° (*picrate*, m. p. about 293°; *chloride*, yellow needles, m. p. 253°, indefinite; *bromide*, m. p. 334°, indefinite; *methiodide*, yellow, prismatic crystals, m. p. about 228—230°; *tri-acetyl* derivative, colourless prisms, m. p. 158° and its *picrate*, yellow needles, m. p. 182°). H. W.

Preparation of Aralkyl Esters of 2-Phenylquinoline-4-carboxylic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 167066).—The aralkyl esters of 2-phenylquinoline-4-carboxylic acid, for example, the benzyl ester, whilst having all the advantages of the alkyl or aryl esters, are, in addition, much better solvents of uric acid. They may be prepared by any of the known methods of esterification. *Benzyl* 2-*phenylquinoline*-4-*carboxylate*, prepared, for example, by the action of 1·25 parts of benzyl chloride on 2·5 parts of the sodium salt of the acid suspended in 10 parts of acetone, forms, after suitable purification, citron-yellow crystals, m. p. 77—78°, insoluble in water, but soluble in hydrochloric acid, ether, benzene, or oils. G. F. M.

Preparation of Disubstituted 2 : 4-Diketotetrahydro-oxazoles. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIARD, P. MONNET & CARTIER (Brit. Pat. 159153).—Disubstituted derivatives of 2 : 4-diketotetrahydro-oxazole of the general formula $\mathrm{RR'C}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CO\cdot NH}\end{matrix}$ are obtained by the action of chloroformic ester on the correspondingly disubstituted glycollamide, preferably in the presence of an alkali carbonate and a neutral organic solvent. For example, 450 grams of phenylethylglycollamide dissolved in 3 litres of toluene, after about three hours' boiling with 700 grams of anhydrous potassium carbonate and 300 grams of ethyl chloroformate added gradually during two hours, give a product from which, on treatment with water and sulphuric acid, a nearly theoretical yield of a crystalline mass of 5 : 5-phenylethyl-2 : 4-diketotetrahydro-oxazole is obtained. This is purified by distillation in a vacuum (b. p. 176°/3 mm.) and the distillate on cooling sets to a crystalline mass, m. p. 63°. These oxazoles are slightly soluble in hot water and form very soluble, well characterised salts when neutralised with the hydroxides or carbonates of the alkalis or alkaline earths. They have hypnotic and narcotic properties.

G. F. M.

A Comparison of some Isomeric *iso*Cyanines. FRANCES MARY HAMER (T., 1921, **119**, 1432—1444).

Constitution of the Cyanines. W. KÖNIG and O. TREICHEL (*J. pr. Chem.*, 1921, **102**, 63—84).—The presence of two intact quinoline rings in the cyanines and *iso*cyanines was originally formulated by König (A., 1906, i, 207) and largely confirmed by the work of Kaufmann (A., 1911, i, 328; 1912, i, 502). Certain considerations, which are fully outlined in the original, had led König (A., 1912, i, 729) to take into consideration alternative formulæ in which one of the quinoline nuclei has suffered fission of the pyridine ring, and in accordance with which the cyanines and *iso*cyanines are to be regarded as condensation products of monoalkylaminocinnamaldehydes with quinaldinium or lepidinium salts. The authors have therefore endeavoured to prepare synthetically dialkylated substances of the latter type for purposes of spectroscopic and chemical comparison with the cyanines and *iso*cyanines. This aim has not been completely achieved owing to the inability to obtain *o*-dimethylaminocinnamaldehyde. It is shown, however, that the absorption curve, in the ultra-violet, of a solution of *p*-dimethylaminocinnamylidenequinaldine methoperchlorate decolorised by hydrochloric acid is widely different from that of a similar solution of *iso*cyanine, and that the latter cannot therefore have the " chain " structure. Moreover, since *p*- and *o*-dimethylaminobenzylidenequinaldine methoperchlorates show identical ultra-violet absorption curves (after being decolorised by hydrochloric acid), it follows by analogy that the cyanines also do not contain the open chain. This result is in complete harmony with the observations of Mills and Evans (T., 1920, **117**, 1035).

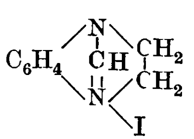
The scope of the investigation has been extended so as to include the examination of a series of condensation products of dimethylaminobenzaldehyde and dimethylaminocinnamaldehyde with α- and γ-methyl*cyclo*ammonium salts. The authors are drawn to the conclusions that (1) *o*-dimethylamino-compounds are not true dyes to the same extent as the corresponding para-derivatives, the absorption curves of which have a much more selective character; (2) the substitution of the α′-phenyl-α-methylpyridine residue for the quinaldine residue has a marked hypsochromic effect; (3) the replacement of a cyclic vinylene group by a sulphur atom has little influence on the absorption; (4) the streptostatic introduction of the vinylene group causes a displacement of the maximum of absorption towards the region of longer wave-length without materially altering the form of the curve.

The following individual substances are described: 4-*methylquinoline methoperchlorate*, m. p. 153°; 6-*phenyl*-2-*methylpyridine methoperchlorate*, colourless needles, m. p. 178°; *benzothiazole methoperchlorate*, m. p. 149°; 1-*methylbenzothiazole methoperchlorate*, m. p. 126°; p-*dimethylaminobenzylidene*-2-*methylquinoline methoperchlorate*, red plates, m. p. 274°, and its *hydrogen perchlorate*, brown needles, m. p. 231°; p-*dimethylaminobenzylidene*-2-*methylquinoline ethiodide*, prisms, m. p. 249°; p-*dimethylaminobenzylidene*-4-*methylquinoline methoperchlorate*, green prisms, m. p. 233°; p-*dimethyl-*

aminobenzylidene-1-*methylbenzothiazole methoperchlorate*, red needles, m. p. 245°; p-*dimethylaminobenzylidene*-6-*phenyl*-2-*methylpyridine methoperchlorate*, yellowish-red needles, m. p. 189°; o-*dimethylaminobenzylidene*-2-*methylquinoline methoperchlorate*, red needles, m. p. 186°; o-*dimethylaminobenzylidene*-1-*methylbenzothiazole methoperchlorate*, red leaflets, m. p. 184°; p-*dimethylaminocinnamylidene*-2-*methylquinoline methoperchlorate*, lustrous, green crystals, m. p. 243°; p-*dimethylaminocinnamylidene*-1-*methylbenzothiazole methoperchlorate*, m. p. 244°; *methyl*iso*cyanine perchlorate*, needles, decomp. above 210°. The dyes are generally prepared by the protracted heating of solutions of molar amounts of the components in methyl or ethyl alcohol in the presence of piperidine as catalyst; in certain cases, acetic anhydride is to be preferred to the latter. H. W.

Pyro-condensations in the Pyridine Series. HANS MEYER and ALICE HOFMANN-MEYER (*J. pr. Chem.*, 1921, **102**, 287—294; cf. A., 1917, i, 641; 1918, i, 66).—Pyridine is decomposed at a bright red heat, yielding mainly 2 : 2′-dipyridyl, m. p. 69°, small quantities of 2 : 3′- and 2 : 4′-dipyridyl being also formed. The only product from 2-methylpyridine which could be characterised definitely is 6 : 6′-dimethyl 2 : 2′-dipyridyl, but oxidation of the crude product shows that pyro-condensation in this case, in contrast with that of toluene, results essentially in the union of the nuclei, which is in accordance with the known greater stability of the methyl group in the 2′-position attached to the pyridine nucleus. 2 : 6-Dimethylpyridine gives a *tetramethyldipyridyl*, colourless needles grouped in rosettes, m. p. 55°, of unknown constitution. 2 : 4 : 6-Trimethylpyridine yields a *hexamethyldipyridyl* (*monohydrate*, colourless solid, m. p. 66—69°) and an oil which resembles quinoline in odour, but from which a uniform material could not be isolated. H. W.

1-Vinylbenziminazole. JAKOB MEISENHEIMER and BRUNO WIEGER (*J. pr. Chem.*, 1921, **102**, 45—62).—A record of further attempts to obtain stereoisomeric compounds containing tervalent nitrogen (cf. A., 1920, i, 761). The introduction of a side chain of two or three carbon atoms to one of the nitrogen atoms of tetrahydroquinoxaline proved exceptionally difficult, since only resinous products, from which a homogeneous material could not be isolated, resulted from the application of ethylene bromide, ethylene chlorobromide, glycol chlorohydrin, propylene chlorobromide, or β-chloropropaldehyde acetal. It was also found impossible to protect one of the imino-groups by acetylation or benzoylation, since only the di-substituted products could be prepared. Benziminazole, on the other hand, was successfully transformed into 1-β-iodoethylbenziminazole, $N\lessdot{}^{CH—}_{C_6H_4}\gtrdot N{\cdot}CH_2{\cdot}CH_2I$ which, however, did not



suffer intramolecular alkylation to a compound of the annexed type when treated with alcoholic potassium hydroxide, but lost hydrogen iodide with formation of 1-vinylbenziminazole. The iodide, when heated by itself, undergoes intermolecular alkylation, yielding a polymeride of the desired substance of the type:

$$\text{-NI}{<}{}^{\text{CH}-}_{\text{C}_6\text{H}_4}{>}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NI}{<}{}^{\text{CH}-}_{\text{C}_6\text{H}_4}{>}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NI}{<}{}^{\text{CH}-}_{\text{C}_6\text{H}_4}{>}\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\text{-}$$

Tetrahydroquinoxaline is converted by benzoyl chloride in acetone solution into *dibenzoyltetrahydroquinoxaline*, m. p. 201·5°.

Benziminazole is very readily prepared by the action of formic acid on *o*-phenylenediamine if the initial materials are pure; it gives a *picrate*, slender, golden-yellow needles, m. p. 223°. It can be converted into 1-β-*hydroxyethylbenziminazole* by treatment with an excess of glycol chlorohydrin at the laboratory temperature in the presence of aqueous alkali, by heating the components in toluene solution or, less advantageously, by heating without a solvent. The most satisfactory process, however, consists in the union of benziminazole with ethylene oxide in the presence of a little water, the formation of by-products being almost entirely avoided if the temperature is kept sufficiently low. The crude material is purified by way of the *picrate*, pale yellow needles, m. p. 204°. Pure N-β-hydroxyethylbenziminazole has m. p. 107—108° (*hydrochloride*, coarse, colourless needles, m. p. 183—184°, *platinichloride*, orange-red prisms, m. p. 189—190°). It is converted by boiling fuming hydriodic acid (*d* 1·99) in the presence of red phosphorus into 1-β-*iodoethylbenziminazole hydriodide*, m. p. 174—175° after softening at 170°. The corresponding free *base* is a pale yellow, viscous liquid which, on account of its instability, could not be purified completely; it gives a *picrate*, m. p. 196—197° (decomp.). The hydriodide is converted by boiling methyl alcoholic sodium methoxide solution into 1-*vinylbenziminazole*, b. p. 144—146°/12 mm., which rapidly darkens when exposed to light and air, but can be preserved in a vacuum for a considerable period without change. It is converted by concentrated hydriodic acid into 1-β-iodoethylbenziminazole and by boiling dilute hydrochloric acid into the corresponding ethanol. It gives a *picrate*, m. p. 194—195° (decomp.), and a *platinichloride*, decomp. 240—245°.

1-β-Iodoethylbenziminazole becomes converted at 100° into the colourless, amorphous polymeric *iodide*, m. p. above 360°; the corresponding *picrate* does not melt below 360°. Attempts to isolate a homogeneous free base were unsuccessful. H. W.

spiro-Pyrimidines. II. _cyclo_Hexane-1:5-_spiro_pyrimidines. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1921, **43**, 1366—1370; cf. this vol., i, 360).—α-ε-Dibromopentane was prepared by a slight modification of von Braun's method (cf. A., 1904, i, 841), using phosphorus tribromide and benzoylpiperidine, and subsequently removing the benzonitrile from the dibromopentane by shaking the mixture with cold concentrated sulphuric acid. α-ε-Dibromopentane condenses with ethyl malonate (*loc. cit.*) to give *ethyl* cyclo*hexane*-1 : 1-*dicarboxylate*, b. p. 105—106°/5 mm., the corresponding *amide* having m. p. 237°. The ester condenses with carbamide to give cyclo*hexane*-1 : 5-spiro-2 : 4 : 6-*triketohexahydropyrimidine*, $CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{<}{}^{CO\cdot NH}_{CO\cdot NH}{>}CO$, m. p. 281°,

and with guanidine giving cyclo*hexane*-1 : 5-spiro-2-*imino*-4 : 6-*diketohexahydropyrimidine*. W. G.

Action of Anhydrous Hydrazine on Nitriles. ERNST MÜLLER and LEONHARD HERRDEGEN (*J. pr. Chem.*, 1921, **102**, 113—155).—The action of hydrazine on an extensive series of aliphatic and aromatic nitriles has been investigated. In the former group, the ability to react declines rapidly with increasing molecular weight of the nitrile. The course of the change may be represented by the general scheme :

$$2R{\cdot}C{:}N \xrightarrow{+2H_2N{\cdot}NH_2} 2R{\cdot}C({:}NH){\cdot}NH{\cdot}NH_2 \xrightarrow[-2NH_3]{+NH_2{\cdot}NH_2}$$

$$R{\cdot}C({:}N{\cdot}NH_2){\cdot}NH{\cdot}NH{\cdot}C({:}N{\cdot}NH_2){\cdot}R \xrightarrow{-H_2N{\cdot}NH_2}$$

$$R{\cdot}C{<}\begin{matrix}N\text{———}N\\NH{\cdot}NH\end{matrix}{>}C{\cdot}R \longrightarrow R{\cdot}C{<}\begin{matrix}N\text{——}N\\N(NH_2)\end{matrix}{>}C{\cdot}R.$$

3 : 6-Dimethyldihydro-1 : 2 : 4 : 5-tetrazine and 3 : 6-dimethyltetrazine are prepared by the method of Curtius, Darapsky, and Müller (A., 1916, i, 84); the absorption spectrum of the latter has been investigated. It is hydrolysed by boiling dilute acids in a complicated manner, yielding nitrogen, hydrazine, and acetic acid; the formation of acetaldehyde or ammonia could not be established. Propionitrile and hydrazine slowly yield 3 : 6-*diethyldihydro*-1 : 2 : 4 : 5-*tetrazine*, which was not isolated in the homogeneous condition, and 1-amino-2 : 5-diethyl-1 : 3 : 4-triazole, colourless, silky needles, m. p. 160°. The former is oxidised readily to 3 : 6-*diethyltetrazine*, which could only be obtained as a viscous, red liquid; it is hydrolysed by acid in the same manner as the dimethyl compound. Butyronitrile and hydrazine give the corresponding tetrazine in too small quantity to permit further investigation, whilst *iso*valeronitrile does not react perceptibly with hydrazine, even after protracted heating.

3 : 6-Diphenyldihydrotetrazine, m. p. 191°, is produced from benzonitrile and anhydrous hydrazine readily at 100°, slowly at the atmospheric temperature, and is transformed by nitrous acid into 3 : 6-diphenyltetrazine, m. p. 195°; the latter is hydrolysed by acid with the formation of nitrogen, hydrazine, benzaldehyde, benzoic acid, and 2 : 5-diphenyl-1 : 3 : 4-oxadiazole, m. p. 137—138°, but the relative amounts of these products indicate considerable complexity in the change.

The slow formation of a tetrazine is observed when a mixture of benzyl cyanide and hydrazine is boiled for several days, but the product could not be isolated in substance, 1-amino-2 : 5-dibenzyl-1 : 3 : 4-triazole, m. p. 166·5°, being obtained in its place. The components do not react with one another at the laboratory temperature.

p-Toluonitrile is slowly transformed into di-*p*-tolyldihydrotetrazine, pale yellow needles, m. p. 223°, which is converted by nitrous acid into di-*p*-tolyltetrazine, m. p. 232°. *m*-Toluonitrile readily yields 3 : 6-*di*-m-*tolyldihydro*-1 : 2 : 4 : 5-*tetrazine*, small, golden-yellow needles, m. p. 194—195°, after darkening above 159°, which is hydrolysed by concentrated hydrochloric acid initially to hydrazine chloride and

2 : 5-di-*m*-tolyl-1 : 3 : 4-oxadiazole, m. p. 72—73°, after softening at 67°, and ultimately to hydrazine and *m*-toluic acid. It is readily oxidised to 3 : 6-*di*-m-*tolyl*-1 : 2 : 4 : 5-*tetrazine*, red needles, m. p. 150—152°, which is converted by boiling dilute acid into nitrogen, hydrazine, and *m*-toluic acid, *m*-tolualdehyde appearing not to be formed. Protracted ebullition of a mixture of *m*-toluonitrile and anhydrous hydrazine leads to the production of 1-amino-2 : 5-di-*m*-tolyl-1 : 3 : 4-triazole, colourless leaflets, m. p. 176—177° (decomp.). *o*-Toluonitrile, on the other hand, does not appear to react with anhydrous hydrazine.

β-Naphthonitrile reacts in the same manner as *p*-toluonitrile, yielding 3 : 6-di-β-naphthyldihydrotetrazine, slender, yellow needles, m. p. 239—240°, which is readily transformed into 3 : 6-di-β-naphthyltetrazine, red crystals, m. p. 249°; the dihydro-compound is converted by boiling acids, to a small extent only, into hydrazine and β-naphthoic acid, the main hydrolysis occurring in the direction of hydrazine and 2 : 5-*di*-β-*naphthyl*-1 : 3 : 4-*oxadiazole*, m. p. 210—211°.

When absolute hydrocyanic acid and anhydrous hydrazine are mixed very cautiously at the temperature of a freezing mixture, the very unstable *diammonium cyanide*, $N_2H_5{\cdot}CN$, is obtained as a colourless, crystalline mass, m. p. 17° (cf. Franzen and Lucking, A., 1911, ii, 285). If it is melted and subsequently heated to 55°, a yellow liquid is produced which solidifies in a vacuum to a yellow, crystalline *substance*, probably dimethinehydrazodihydrazone, $NH_2{\cdot}N{:}CH{\cdot}NH{\cdot}NH{\cdot}CH{:}N{\cdot}NH_2$, formed in accordance with the scheme $CH({:}NH){\cdot}NH{\cdot}NH_2 \xrightarrow[-NH_3]{+N_2H_4} CH({:}N{\cdot}NH_2){\cdot}NH{\cdot}NH_2 +$ $CH({:}NH){\cdot}NH{\cdot}NH_2 \xrightarrow{-NH_3} NH_2{\cdot}N{:}CH{\cdot}NH{\cdot}NH{\cdot}CH{:}N{\cdot}NH_2$. The main evidence of its constitution rests on its conversion into a *benzylidene* derivative, m. p. 99°, after softening at 94°, of approximately the expected composition. When the dimethine compound is treated with sodium nitrite and acetic acid, it is converted into 1 : 2 : 4 : 5-tetrazine, which, on reduction with zinc dust in ethereal solution, passes into dihydrotetrazine, m. p. 117—119°, whereas Curtius, Darapsky, and Müller (*loc. cit.*) give m. p. 125—126°. 1-Amino-1 : 3 : 4-triazole, m. p. 83°, is formed when diammonium cyanide is heated at 120° until ammonia is no longer evolved. H. W.

Reduction of Aromatic Azo-compounds and Nitro-compounds. TOM SIDNEY MOORE (Brit. Pat. 165838).—Aromatic azo-compounds and nitro-compounds are reduced to amines by the action of a relatively large quantity of iron filings or borings in presence of water and a relatively small quantity of sulphur dioxide, considerably less than would be required to generate a quantity of ferrous hyposulphite sufficient to effect the reduction. For example, *p*-nitrophenol (1 part) is reduced to *p*-aminophenol by boiling with 4 parts of iron and 5 parts of water, 0·2 part of sulphurous acid in aqueous solution being gradually added during one hour. When reduction is complete, sodium carbonate and sulphite are added, and the boiling solution is separated from the

iron sludge by filtration. White crystals of the amine are deposited from the filtrate, and the total yield amounts to about 80% of the theoretical. The probable course of the reaction is not indicated. In a similar way, *p*-aminophenol and sulphanilic acid are obtained by the reduction of sodium *p*-hydroxyazobenzene-*p*-sulphonate, 2 : 4-diaminophenol from dinitrophenol, the phenylenediamines from the nitroanilines, etc. G. F. M.

Isonitriles. I. Compound of *p*-*iso*Nitriloazobenzene [*p*-Carbylaminoazobenzene]. M. PASSERINI (*Gazzetta*, 1921, **51**, ii, 126—129).—When *p*-carbylaminoazobenzene is treated, in acetone solution, with acetic acid and hydrogen peroxide (this vol., i, 197), confinement of the oxidising action solely to the *iso*-nitrilo-group takes place to only a very small extent; the reaction yields, indeed, a very small proportion of 4 : 4′-carbaminoazobenzene, which is evidently formed by the action of the water, introduced with the hydrogen peroxide, on the azobenzene *p*-carbimide formed by oxidation of the *iso*nitrile. The principal product of the reaction consists of the acetyl derivative of hydroxy*iso*butyryl-*p*-aminoazobenzene, $NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CMe_2{\cdot}OAc$, m. p. 147—148°; the formation of this compound, which yields hydroxy*iso*butyryl-*p*-aminoazobenzene on hydrolysis, is probably preceded by that of a labile additive compound of acetic acid and acetone, $OH{\cdot}CMe_2{\cdot}OAc$, this then reacting with the *iso*nitrile; that the acetone does not act first as hydrate and the acetic acid subsequently is shown by the fact that the reaction takes place in a medium as nearly dry as possible and by the difficulty experienced in acetylating the hydrolysed product.

The compound, m. p. 222—223°, obtained from benzaldehyde and *p*-carbylaminoazobenzene, and previously regarded as an additive compound (*loc. cit.*), is probably of similar structure to that given by acetic acid, its formation being due to the presence of benzoic acid in the aldehyde used; an increased yield is, indeed, obtained when benzoic acid is employed in place of benzaldehyde. T. H. P.

The Action of Diazonium Salts on Benzene- and *p*-Toluenesulphonyl Derivatives of Acetic Acid, Ethyl Acetate, Acetonitrile, and Acetamide. J. TRÖGER and A. BERNDT (*J. pr. Chem.*, 1921, **102**, 1—35).—The addition of a solution of benzenediazonium chloride to benzenesulphonylacetonitrile dissolved in the equivalent quantity of aqueous sodium hydroxide or to an alcoholic solution of the nitrile in the presence of concentrated aqueous sodium acetate solution leads to the formation of *benzenesulphonylbenzeneazoacetonitrile*, $SO_2Ph{\cdot}CH({\cdot}N_2,Ph){\cdot}CN$, or the *phenylhydrazone* of *benzenesulphonylformyl cyanide*,

$$SO_2Ph{\cdot}C({:}N{\cdot}NHPh){\cdot}CN,$$

golden-yellow, prismatic needles, m. p. 160° [the *sodium* salt, yellow, quadratic leaflets ($+2H_2O$), *potassium*, *lead*, and *silver* salts of which were analysed]. Similar methods lead to the production of the following substances which, for the sake of brevity, are cited as azo-compounds, although the possibility of their hydrazone nature

is by no means excluded : *benzenesulphonyl*-m-*tolueneazoacetonitrile*, coarse, dark-red needles, m. p. 153—154°, and its *sodium* (+$2H_2O$), *potassium*, *lead*, and *silver* salts; *benzenesulphonyl*-o-*tolueneazoacetonitrile*, yellow or brownish-red crystals, m. p. 154°, and its *sodium* and *potassium* salts, which can be prepared in the absence of water; *benzenesulphonyl*-p-*tolueneazoacetonitrile*, red, prismatic needles, m. p. 172°, and its *sodium* (+$2H_2O$), *potassium*, *lead*, and *silver* salts; *benzenesulphonyl*-o-*methoxybenzeneazoacetonitrile*, small, rust-brown needles, m. p. 165°, and its *sodium*, *potassium*, *lead*, and *silver* salts; *benzenesulphonyl*-p-*methoxybenzeneazoacetonitrile*, small, pale yellow needles, m. p. 159°, and its *sodium* and *potassium* salts; *benzenesulphonyl*-as-m-*xyleneazoacetonitrile*, brownish-red leaflets, m. p. 164—165°, and its *sodium*, *potassium*, *lead*, and *silver* salts; *benzenesulphonyl*-p-*ethoxybenzeneazoacetonitrile*, ruby-red needles, m. p. 173°, and its *sodium*, *potassium* (+$2H_2O$), *lead*, and *silver* salts; p-*toluenesulphonylbenzeneazoacetonitrile*, golden-yellow, lustrous needles, m. p. 144°, the alkali salts of which could not be isolated, even in the absence of water; p-*toluenesulphonyl*-o-*tolueneazoacetonitrile*, small, greenish-yellow, prismatic needles, m. p. 152°, the alkali salts of which could not be isolated; p-*toluenesulphonyl*-m-*tolueneazoacetonitrile*, yellowish-brown prisms, m. p. 135°, and its *sodium* salt (+$2H_2O$); p-*toluenesulphonyl*-p-*tolueneazoacetonitrile*, yellow, prismatic needles, m. p. 154°, and its *sodium* salt (+$2H_2O$); p-*toluenesulphonyl*-o-*methoxybenzeneazoacetonitrile*, yellow, prismatic needles, m. p. 176°, and its *sodium* salt (+$2H_2O$); p-*toluenesulphonyl*-p-*methoxybenzeneazoacetonitrile*, egg-yellow crystals, m. p. 145°, and its oily *sodium* and *potassium* (+H_2O) salts; p-*toluenesulphonyl*-p-*ethoxybenzeneazoacetonitrile*, prisms, m. p. 143°; p-*toluenesulphonyl*-as-m-*xyleneazoacetonitrile*, pale yellow crystals, m. p. 151°.

All the nitriles described above are unusually stable towards hydrolysing agents, and it was not found possible to secure conditions under which the cyano- was converted into the carboxyl group without profound change in the remainder of the molecule. In the hope of securing a path to the acids, the action of diazonium salts of the benzene- and *p*-toluene-sulphonyl derivatives of ethyl acetate was therefore investigated. In this case, the sodium acetate method is not applicable, and the following compounds were prepared by the neutralisation of the mineral acid liberated during coupling by cautious addition of sodium hydroxide solution: *ethyl benzenesulphonylbenzeneazoacetate*, $SO_2Ph{\cdot}CH({\cdot}N_2Ph){\cdot}CO_2Et$, or the *phenylhydrazone* of *ethyl benzenesulphonylglyoxylate*,

$$SO_2Ph{\cdot}C(N{\cdot}NHPh){\cdot}CO_2Et,$$

yellow prisms, m. p. 140°, and its *sodium* salt, which can be prepared only in the absence of water; *ethyl benzenesulphonyl*-p-*tolueneazoacetate*, dark yellow, prismatic needles, m. p. 128°; *ethyl benzenesulphonyl*-m-*tolueneazoacetate*, small, pale yellow needles, m. p. 102°; *ethyl benzenesulphonyl*-o-*tolueneazoacetate*, reddish-yellow prisms, m. p. 120°; *ethyl benzenesulphonyl*-p-*methoxybenzeneazoacetate*, reddish-brown prisms, m. p. 147°; *ethyl benzenesulphonyl*-o-*methoxybenzeneazoacetate*, greenish-yellow, silky leaflets,

m. p. 143°; *ethyl benzenesulphonyl*-p-*ethoxybenzeneazoacetate*, small prisms, m. p. 134°; *ethyl benzenesulphonyl*-as-m-*xyleneazoacetate*, reddish-yellow leaflets, m. p. 146°, and its *sodium* salt; *ethyl* p-*toluenesulphonylbenzeneazoacetate*, orange-yellow needles, m. p. 134°; *ethyl* p-*toluenesulphonyl*-p-*tolueneazoacetate*, dark orange crystals, m. p. 129°; *ethyl* p-*toluenesulphonyl*-m-*tolueneazoacetate*, pale brown prisms, m. p. 155°; *ethyl* p-*toluenesulphonyl*-o-*tolueneazoacetate*, slender, yellow prisms, m. p. 132°, and its *sodium* salt; *ethyl* p-*toluenesulphonyl*-o-*methoxybenzeneazoacetate*, dark green, silky needles, m. p. 157°; *ethyl* p-*toluenesulphonyl*-p-*methoxybenzeneazoacetate*, greenish-brown prisms, m. p. 144°; *ethyl* p-*toluenesulphonyl*-p-*ethoxybenzeneazoacetate*, reddish-brown crystals, m. p. 140°; *ethyl* p-*toluenesulphonyl*-as-m-*xyleneazoacetate*, tile-red prisms, m. p. 159°, and its *sodium* salt.

Attempts to isolate uniform products by the hydrolysis of the esters just described were not successful, and the preparation of the acetamide derivatives was therefore undertaken. In this instance, the use of sodium acetate and sodium hydroxide respectively leads to the formation of different substances of the same percentage composition; it is considered, with some reserve, that the products obtained by the former method are analogous with those from the nitrile or ester. The following individuals are described: *benzenesulphonylbenzeneazoacetamide*,

$$SO_2Ph{\cdot}CH(N_2Ph){\cdot}CO{\cdot}NH_2,$$

or the *phenylhydrazone* of *benzenesulphonylglyoxylamide*,

$$SO_2Ph{\cdot}C(N{\cdot}NHPh){\cdot}CO{\cdot}NH_2,$$

yellowish-brown crystals, m. p. 158°, and its *sodium* salt; *benzenesulphonyl*-m-*tolueneazoacetamide*, reddish-brown, pointed needles, m. p. 152°, and its *sodium* salt; *benzenesulphonyl*-o-*tolueneazoacetamide*, slender, pale-yellow needles, m. p. 181°; *benzenesulphonyl*-p-*tolueneazoacetamide*, tile-red, prismatic needles, m. p. 195°; *benzenesulphonyl*-p-*methoxybenzeneazoacetamide*, reddish-yellow, quadratic crystals, m. p. 151°; *benzenesulphonyl*-o-*methoxybenzeneazoacetamide*, golden-yellow needles, m. p. 162°; *benzenesulphonyl*-p-*ethoxybenzeneazoacetamide*, pale yellow, quadratic crystals, m. p. 174°; *benzenesulphonyl*-as-m-*xyleneazoacetamide*, golden-yellow, prismatic needles, m. p. 204°; p-*toluenesulphonylbenzeneazoacetamide*, reddish-brown, lustrous prisms, m. p. 134°; p-*toluenesulphonyl*-p-*tolueneazoacetamide*, brownish-red crystals, m. p. 170°; p-*toluenesulphonyl*-m-*tolueneazoacetamide*, yellowish-brown crystals, m. p. 158°; p-*toluenesulphonyl*-o-*tolueneazoacetamide*, yellow needles, m. p. 169°; p-*toluenesulphonyl*-p-*methoxybenzeneazoacetamide*, ruby-red needles, m. p. 151°, and its *sodium* salt; p-*toluenesulphonyl*-o *methoxybenzeneazoacetamide*, blood-red crystals, m. p. 162°; p-*toluenesulphonyl*-p-*ethoxybenzeneazoacetamide*, blood-red crystals, m. p. 164°; p-*toluenesulphonyl*-as-m-*xyleneazoacetamide*, brownish-yellow prisms, m. p. 200°. The hydrolysis of these amides has not been studied completely.

The following products are obtained by the use of sodium hydroxide for neutralisation of the acid liberated during coupling (cf. above); their constitution has not been elucidated: *compound*,

$C_{15}H_{15}O_3N_3S$ (from benzenesulphonylacetamide and *o*-toluenediazonium chloride), red, prismatic needles, m. p. 190°; *compound*, $C_{15}H_{15}O_3N_3S$ (from *p*-toluenesulphonylacetamide and benzenediazonium chloride), brownish-red, prismatic leaflets, m. p. 160°; *compound*, $C_{16}H_{17}O_3N_3S$ (from *p*-toluenesulphonylacetamide and *o*-toluenediazonium chloride), tile-red needles, m. p. 178°; *compound*, $C_{16}H_{17}O_4N_3S$ (from *p*-toluenesulphonylacetamide and diazotised *o*-anisidine), dark red, iridescent needles, m. p. 200°.

The action of solutions of diazonium salts on the free acids follows a complex course which depends, in part, at any rate, on the use of sodium hydroxide or sodium acetate for the removal of liberated mineral acid. With the former reagent, it is established that elimination of the $R\cdot SO_2\cdot$ group does not take place and that compounds of the type, $SO_2R\cdot C(N\cdot NHR)\cdot CO_2H$, or

$$SO_2R\cdot CH\colon N\cdot NHR,$$

are formed with difficulty or not at all. Formazyl compounds, or mixtures of the latter and hydrazones, are produced. In a large number of instances exceptional experimental difficulties are encountered owing to the absence of a suitable solvent or the impossibility of separating the complex products into their individual components. The *formazyl* compound,

$$SO_2Ph\cdot C(N\cdot NH\cdot C_7H_7)\cdot N_2\cdot C_7H_7,$$

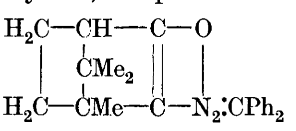
dark red leaflets, m. p. 161°, could, however, be isolated from benzenesulphonylacetic acid and two or more molecular proportions of *o*-toluenediazonium salt, whilst a similar *compound*,

$$SO_2Ph\cdot C(N\cdot NH\cdot C_6H_4\cdot OMe)\cdot N_2\cdot C_6H_4\cdot OMe,$$

slender, greenish-red needles, m. p. 197°, is prepared by the use of diazotised *o*-anisidine. In the presence of sodium acetate, benzenediazonium chloride yields with benzene- or *p*-toluene-sulphonylacetic acid a *compound*, brown needles, m. p. 135°, which is free from sulphur; its constitution has not been elucidated. In a similar manner, benzenesulphonylacetic acid and *o*-toluenediazonium chloride give a sulphur-free *product*, slender, brown needles, m. p. 146°. H. W.

Hydrazones and Azines. II. Condensation Products of Aromatic Ketohydrazones with Orthoquinones. OTTO GERHARDT (*Monatsh.*, 1921, **42**, 63—72; cf. A., 1920, i, 766).—It has been shown previously that little connexion between colour and constitution is exhibited by ketazines, but the formation of intensely coloured products is to be expected by the union of the azomethylene group, $\colon C\colon N_2\colon$, with quinonoid nuclei. The behaviour of aromatic ketazines towards quinones has therefore been investigated. With *p*-benzoquinone and α-naphthaquinone, the main result consists in the oxidation of the ketazine with formation of indefinite products. With more complex orthoquinones, on the other hand, the oxidising action is but little in evidence, and, of the possible reactions, $CR'_2\colon N\cdot NH_2 + O\colon R\colon O \longrightarrow CR'_2\colon N\cdot N\colon R\colon O$ and $2CR'_2\colon N\cdot NH_2 + O\colon R\colon O \longrightarrow CR'_2\colon N\cdot N\colon R\colon N\cdot N\colon CR'_2$, it has been found possible to realise the first, but not the second. The condensation products, for which the term "quinaketazines" is

proposed, are generally prepared in good yield by boiling a solution of molar quantities of the components in a dry hydrocarbon of the benzene series. The following individuals are described. *Phenanthrenequinobenzophenoneketazine*, $C_6H_4{<}{\begin{smallmatrix}CO-\\C_6H_4\end{smallmatrix}}{>}C{:}N_2{:}CPh_2$, dark red crystals, m. p. 158—159°; *phenanthrenequinofluorenoneketazine*, brownish-violet crystals, m. p. 215—216°; *acenaphthenequinobenzophenoneketazine*, yellow crystals, m. p. 185—186°; *isatobenzophenoneketazine*, $NH{<}{\begin{smallmatrix}CO-\\C_6H_4\end{smallmatrix}}{>}C{:}N_2{:}CPh_2$, canary-yellow crystals, m. p. 214—215°; *acenaphthenequinofluorenoneketazine*, brownish-yellow crystals, m. p. 193·5—195°; *isatofluorenoneketazine*, slender, cinnabar-red crystals, m. p. 185—186°; *thionaphthenequinobenzophenoneketazine*, $S{<}{\begin{smallmatrix}CO-\\C_6H_4\end{smallmatrix}}{>}C{:}N_2{:}CPh_2$, lustrous, cinnabar-red crystals, m. p. 107—108·5°; *thionaphthenequinofluorenoneketazine*, dark red needles, m. p. 221—223°; *camphorquinobenzophenoneketazine* (annexed formula), almost colourless, crystalline powder, m. p. 106·5—108°; *camphorquinofluorenoneketazine*, a colourless, crystalline powder, m. p. 156—157°. H. W.



Preparation of Nitro-derivatives of β-Azides of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 337734; from *Chem. Zentr.*, 1921, iv, 262).—β-Azides of the anthraquinone series are treated with strong nitric acid or nitric and sulphuric acids. The nitro-group enters the α-position next to the azide group. 1-*Nitro-2-azidoanthraquinone*, prepared by the action of fuming nitric acid on 2-azidoanthraquinone, forms yellowish-green crystals becoming light orange-red on exposure to light and air, m. p. 210° (decomp.). On heating an aqueous suspension with sodium sulphide, the colour becomes green and then violet, and by further heating 1 : 2-diaminoanthraquinone crystallises out with evolution of nitrogen. By addition of 2 : 6-diazidoanthraquinone to cold fuming nitric acid or a solution of potassium nitrate in strong sulphuric acid with cooling, 1 : 5-*dinitro*-2 : 6-*diazidoanthraquinone* separates in yellow crystals which, after recrystallisation from nitrobenzene, form light yellow needles, m. p. 200°; at 202°, sudden decomposition takes place with separation of carbon. Reduction with sodium sulphide gives 1 : 2 : 5 : 6-*tetraminoanthraquinone*. G. W. R.

The Hydrazide and Azide of Benzylsulphonic Acid. THEODOR CURTIUS and FRIEDRICH WILHELM HAAS (*J. pr. Chem.*, 1921, **102**, 85—112).—The substances named in the title have been prepared as examples of this class of compounds in which the sulphonhydrazide and sulphonazide groups are attached to an aromatic radicle instead of directly to an aromatic nucleus. In general, they show a close resemblance to the corresponding compounds of benzenesulphonic acid (cf. Curtius and Rissom, *Zeitsch. angew. Chem.*, 1913, **26**, [iii], 134).

Benzylsulphonhydrazide, $CH_2Ph \cdot SO_2 \cdot NH \cdot NH_2$, colourless crystals, m. p. 131—132° (decomp.), is obtained by the action of hydrazine hydrate on benzylsulphonyl chloride in cold, absolute alcoholic solution. It decomposes in boiling aqueous solution into nitrogen, hydrogen, and benzylsulphinic acid, but attempts to isolate di-imide (which is presumably formed intermediately during the reaction) in the form of its silver salt were unsuccessful. When silver nitrate is added to solutions from which much gas has been evolved, a precipitate is formed which blackens rapidly; when, however, the reagent is added to a slightly decomposed solution, the *salt*, $(CH_2Ph \cdot SO_2 \cdot NH \cdot NH_2)_2,AgNO_3$, is precipitated in colourless leaflets. Benzylsulphonhydrazide gives a *hydrochloride*, small, colourless needles, m. p. 148° (decomp.), and a *benzylidene* derivative, $CH_2Ph \cdot SO_2 \cdot NH \cdot N \colon CHPh$, colourless needles, m. p. 139·5° (decomp.). When subjected to protracted heating in almost absolute alcoholic solution it gives *diammonium benzylsulphonate*, $CH_2Ph \cdot SO_3 \cdot N_2H_5$, colourless needles, decomp. about 150°, benzylsulphinic acid, nitrogen, and hydrogen.

Benzylsulphonazide, $CH_2Ph \cdot SO_2 \cdot N_3$, colourless, slender needles, m. p. 54°, is prepared by the action of nitrous acid on the corresponding hydrazide or from benzylsulphonyl chloride and sodium azide in alcoholic solution. When heated with hydrocarbons, it behaves in a similar manner to benzenesulphonazide, evolving two-thirds of its nitrogen and leaving a residue, $CH_2Ph \cdot SO_2 \cdot N<$, which unites with the solvent. With boiling toluene, reaction is very slow, but with *p*-xylene, *benzylsulphon*-p-*xylidide*, $CH_2Ph \cdot SO_2 \cdot NH \cdot C_6H_3Me_2$, pale yellow needles, m. p. 124°; the latter is hydrolysed by concentrated hydrochloric acid to *p*-xylidine, toluene, and sulphur dioxide. The occurrence of the latter is surprising, since the formation of sulphuric acid would be expected; the presence of benzyl chloride or benzyl alcohol in the toluene, which would account for the reaction, could not be demonstrated. Similarly, benzylsulphonazide and naphthalene give *benzylsulphon-α-naphthalide*, yellow needles, m. p. 146°, which is identical in all respects with the synthetic product (*benzylsulphon-β-naphthalide* crystallises in needles, m. p. 148·5°); it is hydrolysed by hydrochloric acid to α-naphthylamine hydrochloride, sulphur dioxide, and resinous matter, which doubtless originates from benzyl alcohol.

Two reactions occur concurrently when benzylsulphonazide is heated with aniline. The first of these leads to the formation of hydrazoic acid and *benzylsulphonanilide*, colourless needles, m. p. 102°, in accordance with the equation $CH_2Ph \cdot SO_2 \cdot N_3 + NH_2Ph = CH_2Ph \cdot SO_2 \cdot NHPh + N_3H$, whilst the second gives rise to the residue, $CH_2Ph \cdot SO_2 \cdot N \colon$ which combines with two atoms of hydrogen, yielding benzylsulphonamide. Since the hydrogen atoms are derived from aniline, it was expected that benzidine would be formed as anti-substance, but no trace of this substance could be detected. On the other hand, considerable quantities of *pp'*-diaminotriphenylmethane are formed which originate in the following manner. In addition to the usual action which leads to the normal anilide, benzylsulphonazide decomposes in accordance with the scheme

$CH_2Ph \cdot SO_2 \cdot N_3 = Ph \cdot CH\colon + SO_2 + N_3H$; the residue, $Ph \cdot CH\colon$, unites subsequently with two of the aniline residues liberated by the formation of the sulphonamide according to the equation $CH_2Ph \cdot SO_2 \cdot N_3 + 2Ph \cdot NH_2 = CH_2Ph \cdot SO_2 \cdot NH_2 + N_2 + 2NH_2 \cdot C_6H_4 \cdot$, thus giving *pp'*-diaminotriphenylmethane. It is noticeable that the reaction $CH_2Ph \cdot SO_2 \cdot N_3 + Ph \cdot NH_2 = CH_2Ph \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot NH_2 + N_2$ does not appear to take place, although this is the main change suffered by benzenesulphonazide.

The main product of the action of benzylsulphonazide on dimethylaniline is *benzylsulphonaminodimethylaniline*,

$$CH_2Ph \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot NMe_2,$$

colourless crystals, m. p. 127°; the definite melting point of the crude product indicates that it is homogeneous and, probably, the para-derivative. As by-products, sulphur dioxide, hydrazoic acid, ammonium hydrazoate, and *pp'*-tetramethyldiaminotriphenylmethane are obtained. H. W.

A New Method for the Preparation of α-Acylphenylhydrazines. WALLACE FRANK SHORT (T., 1921, **119**, 1445—1448).

Decomposition of Aldehydo-phenylhydrazones. R. CIUSA (*Gazzetta*, 1921, **51**, ii, 125).—The catalytic reduction of aldehydophenylhydrazones into aniline and the nitrile corresponding with the nitrile observed by Mailhe (this vol., i, 463) occurs also when such phenylhydrazones are heated with certain metallic chlorides (Arbuzov, A., 1913, i, 347), and the present author gave the formation of benzonitrile and aniline when benzaldehydephenylhydrazone is heated with zinc chloride as an illustration of the analogy existing between the oximes and hydrazones (A., 1908, i, 833). T. H. P.

The Albumin of the White of Hens' Eggs. S. P. L. SÖRENSEN (*Bull. Soc. chim.*, 1921, [iv], **29**, 593—624).—A lecture delivered before the Chemical Society of France on May 13, 1921. A. A. E.

The Preparation and Recrystallisation of Oxyhæmoglobin. HAROLD WARD DUDLEY and CHARLES LOVATT EVANS (*Biochem. J.*, 1921, **15**, 487—488).—Defibrinated horse blood is centrifuged and the corpuscles are washed with normal saline solution until the washings give no turbidity on boiling. The corpuscles are then dialysed in collodion tubes under pressure against tap and distilled water. The laked corpuscles are centrifuged and the hæmoglobin solution is re-oxygenated. The less soluble oxyhæmoglobin crystallises out suddenly after about twenty minutes. For recrystallisation, the crystals are suspended in 2—3 volumes of water and warmed to 37° in a vacuum, when a clear hæmoglobin solution results. On again passing oxygen into the cooled solution, the oxyhæmoglobin crystallises once more. G. B.

Osmosis and Swelling of Gelatin. C. R. SMITH (*J. Amer. Chem. Soc.*, 1921, **43**, 1350–1366).—Gelatin, free from ash, was used in the experimental work. It was prepared by extracting finely-powdered gelatin in a filter with 10% sodium chloride solution containing about 5 c.c. of concentrated hydrochloric acid per litre until the washings showed no reaction for calcium. The

washing was then continued with 1% sodium chloride solution without acid, the concentration of the solution being diminished as rapidly as control of the swelling would permit. Final washing was effected with distilled water, until the washings were free from chlorides, when 90% alcohol was poured through the mass, which was finally dried in an oven.

The osmotic pressure of this gelatin in the presence of water is proportional to concentration and gives a molecular weight of 96,000, assuming the applicability of the gas laws. Gelatin sols in a collodion membrane immersed in isohydric solutions of univalent acids, or multivalent acids ionising as univalent acids, produce the same osmotic pressure. Similarly, in univalent bases the same osmotic pressure is produced at the same hydroxyl-ion concentration. Minimum osmotic pressure is produced at the isoelectric point where it is not combined with acids or bases and with increasing hydrogen- or hydroxyl-ion concentration the osmotic pressure increases to a maximum and then diminishes. For 0·5 gram of gelatin in 100 c.c. at 10° in univalent acids the maximum osmotic pressure of 158 mm. of water is reached at a hydrogen-ion concentration of $0{\cdot}8-1{\cdot}0\times10^{-3}$. In bases, the maximum pressure of 165 mm. is reached at $0{\cdot}2\times10^{-3}$ hydroxyl-ion concentration. In bivalent acids or bases ionising as such the maximum osmotic pressure is reached at the same hydrogen- or hydroxyl-ion concentration as with univalent acids or bases respectively, but is only about 55 mm. of water.

When immersed in univalent acids, dry gelatin combines with equivalent amounts at the same hydrogen-ion concentration, and the amount of swelling is approximately the same for all. The maximum swelling occurs at about 4×10^{-3} hydrogen-ion concentration, when one gram of air-dry gelatin occupies a volume of about 46 c.c. Bivalent ionising acids give much less swelling with a maximum at about the same point. Salt-ions do not combine with gelatin, but increase the absorption of alkalis or acids. They markedly decrease swelling and osmotic pressure. The swelling of gelatin is the result of osmotic pressure within the jelly, with the jelly acting as an imperfectly resisting membrane, the more so when highly swollen. Whilst the osmotic pressure at the optimum concentration of univalent acids and bases is the same, the swelling is much less in alkalis because of the weakened membrane effect. Bivalent sulphuric acid gives the same swelling as bivalent calcium or barium hydroxide when swelling is small and the solution is not so great. W. G.

Digestion of Fibrin and Caseinogen by Trypsin. EDWARD STAFFORD EDIE (*Biochem. J.*, 1921, **15**, 498—506).—Like alcohol (Edie, A., 1919, i, 460), heat and acids destroy the power of trypsin to digest fibrin more rapidly than its power to digest caseinogen; there seem to be two proteolytic enzymes. The milk coagulating and the proteolytic powers of pancreatic extracts are not in a constant ratio and the former is more thermolabile than the latter. G. B.

Behaviour of Pectin towards Alkalis and Pectase. FRANK TUTIN (*Biochem J.*, 1921, **15**, 494—497; cf. von Fellenberg, A., 1915, i, 774).—Pectin was obtained relatively pure in a yield of 5% from dried apple press cake of the cider press. It neutralised in the cold 1·05% of its weight of sodium hydroxide, but on keeping with excess of alkali a further 12·35% of alkali was neutralised in half an hour. On steam distillation some methyl alcohol and about twice as much acetone are given off. The same amounts of methyl alcohol and acetone are liberated by (clover) pectase, and calcium pectate is formed. Alkalis and pectase are therefore quite similar in action. Both reagents produce pectic acid (containing carbon 39·2—39·4%, hydrogen 5·1%, and neutralising 20·9% of sodium hydroxide). G. B.

The Catalase Reaction. SERGIUS MORGULIS (*J. Biol. Chem.*, 1921, **47**, 341—375).—All the experiments were performed at 20—21°, using a crude catalase preparation obtained from ox-liver. Preliminary experiments indicated that the catalase reaction diminishes both in velocity and in total decomposition of hydrogen peroxide as the acidity increases, the optimum condition being neutrality (P_H 7·0). All further experiments were therefore performed at P_H 6·7 to 6·9, this slight acidity being maintained to prevent the spontaneous decomposition of the peroxide. Using a constant quantity of catalase, a total volume of 50 c.c., and a peroxide concentration varying from 0·8 to 0·40 molar, it was found that with increasing concentration of peroxide the reaction velocity diminishes, the percentage total decomposition decreases, and the total evolution of oxygen increases to a point and then decreases, the maximum evolution corresponding with a total decomposition of peroxide of 65—70%. With the catalase in excess, 100% decomposition results; when the total decomposition falls below 65—70%, further increases in the amount or concentration of the peroxide cause a falling off of the reaction. Between these limits, however, the total oxygen evolved from a constant quantity of peroxide is directly proportional to the amount of catalase used. For concentrations in which the total decomposition of the peroxide is approximately 70%, the reaction is bimolecular; for a total decomposition of about 95% it is unimolecular. The author concludes that a quantitative relation exists between the catalase and peroxide. Below a total decomposition of 65%, the peroxide exercises a depressing influence, a result which he attributes to a reversible reaction; that it is not due to oxidation of the catalase follows from the experimental results. The bearing of the results on the technique of catalase estimations is finally discussed. E. S.

Some Additive Compounds derived from Arsines. GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1921, **119**, 1448—1450).

Derivatives of Sulphur in Commercial Salvarsan. II. HAROLD KING (T., 1921, **119**, 1415—1420).

Preparation of Arsenic Compounds of the Pyrazolone Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 313320; from *Chem. Zentr.*, 1921, iv, 262—263).—Acid groups are introduced into the amino-groups of compounds of the type 1-*p*-arsenodiaryl-di(4-amino-2 : 3-dialkyl-5-pyrazolone). The compounds thus formed, although not markedly poisonous, are strongly bactericidal and may be used in the form of their alkali salts. The products are yellow powders, decomposed by heating with acids. The preparation of some arsenic derivatives of the pyrazolone series is described. 5-*Chloro*-3-*methylpyrazole*-1-*benzene*-4′-*arsinic acid* is obtained by diazotisation of 5-chloro-3-methylpyrazole-1-*p*-aminobenzene, treatment with arsenites, and subsequent acidification; it forms crystals, m. p. 192—195°, when quickly heated, with the formation of an anhydride and subsequently solidifies on elimination of water; it decomposes completely above 290°. 3-*Methyl*-5-*pyrazolone*-1-*benzene*-4′-*arsinic acid* is prepared by diazotisation of *p*-aminophenylarsinic acid, reduction, and condensation with ethyl acetoacetate; it crystallises from hot water and forms a yellow *nitroso*-compound. 2 : 3-Dimethyl-5-pyrazolone-1-benzene-4′-arsinic acid is formed by the methylation of 3-methyl-5-pyrazolone-1-benzene-4′-arsinic acid or the corresponding 5-chloropyrazole derivative; it crystallises from water. By acting on it with sodium nitrite and dilute sulphuric acid, 4-*nitroso*-2 : 3-*dimethyl*-5-*pyrazolone*-1-*benzene*-4′-*arsinic acid* is obtained; it is bluish-green in colour and very unstable; by reduction, 1-p-*arsenodiphenyl*-*di*(4-*amino*-2 : 3-*dimethyl*-5-*pyrazolone*) is obtained. The *hydrochloride* forms yellow crystals. The *monoacetate*, prepared by the action of bromoacetic acid, is a yellow powder. With excess of bromoacetic acid, a *diglycine* is obtained similar to the monoglycine. By the action of formaldehyde sulphoxylate on 1-*p*-arsenodiphenyl-di(4-amino-2 : 3-dimethyl-5-pyrazolone) hydrochloride or 4-nitroso-2 : 3-dimethyl-5-pyrazolone-1-benzene-4′-arsinic acid, 1-p-*arsenodiphenyl*-*di*(4-*amino*-2 : 3-*dimethyl*-5-*pyrazolone*)-*monomethylenesulphoxylate* is obtained as a yellow powder. A *dimethylenesulphoxylate* is obtained when a large excess of formaldehyde sulphoxylate is used. By treating 1-*p*-arsenodiphenyl-di(4-amino-2 : 3-dimethyl-5-pyrazolone) hydrochloride with sodium hydrogen sulphite and formaldehyde the corresponding 4-N-*methylsulphinic acid* compound is obtained as a yellow powder. G. W. R.

Physiological Chemistry.

Respiration and Blood Alkali during Carbon Monoxide Asphyxia. HOWARD W. HAGGARD and YANDELL HENDERSON (*J. Biol. Chem.*, 1921, **47**, 421—431).—The anoxæmia induces excessive breathing (300% or more) which sweeps out the carbon dioxide, and the decrease of blood alkali is an attempt at compensation. After section of the vagi overbreathing and the lowering of the blood alkali do not occur. G. B.

Relation of the Migration of Ions between Cells and Plasma to the Transport of Carbon Dioxide. EDWARD A. DOISY and EMILY P. EATON (*J. Biol. Chem.*, 1921, **47**, 377—393).—The authors have determined the sodium, potassium, chlorine, phosphorus, and bicarbonate content of serum, obtained by centrifuging defibrinated blood, which had been equilibrated with various pressures of carbon dioxide. They find it quite easy to show that increased carbon dioxide content of the plasma produces a shift of hydrochloric acid into the corpuscles; this is what happens during the passage of the blood through the capillaries; since oxygen is given up by the hæmoglobin, the latter becomes less acid and compensates for the hydrochloric acid migrating into the corpuscles. Perhaps phosphate ions also migrate, but the concentration of these and of the sulphuric ions is so small as to make their shift unimportant. Contrary to Hamburger, the authors failed to detect any shift of sodium or potassium, and they regard the blood cells as impermeable to these ions, in agreement with Collip (this vol., i, 379). A tabulation of total molecular concentrations of anions and cations in serum shows an excess of 7% of bases, presumably combined with the protein. G. B.

Distribution of Calcium and Phosphoric Acid in the Blood of Normal Children. MARTHA R. JONES and LILLIAN L. NYE (*J. Biol. Chem.*, 1921, **47**, 321—331).—Estimations were made of the alkali reserve of the plasma, and of the distribution of calcium and phosphoric acid in the blood of children. More phosphoric acid of all types was found in the corpuscles than in the plasma. The unknown phosphoric acid is approximately 70% of the total in the corpuscles, but is negligible in or absent from the plasma. The average calcium content of the corpuscles is slightly less than that of the plasma. E. S.

Mechanism of Anticoagulant Actions [in Blood Clotting]. ANDRÉ GRATIA (*Ann. Inst. Pasteur*, 1921, **35**, 513—557).—The author has been principally concerned with the anticoagulant action of the antithrombins of hirudin and of plasma after peptone injection, and his results support the theory of Schmidt, Morawitz, Bordet, and Delange, rather than those of Nolf and of Howell. Whereas a hirudin solution of 1 : 2500 may be required to prevent the action of ready formed thrombin, a solution of 1 : 10000 will suffice to prevent the activation of prothrombin by kinase. Neutral thrombin-antithrombin mixtures are decomposed at 60° with liberation of antithrombin. This is true of both hirudin and peptone plasma, which differ, however, in other respects (cf. also Dale and Walpole, A., 1916, i, 889). G. B.

The Diffusible Calcium of the Blood Serum. I. Estimation. L. VON MEYSENBUG, A. M. PAPPENHEIMER, T. F. ZUCKER, and MARJORIE F. MURRAY. **II. Human Rickets and Experimental Dog Tetany.** L. VON MEYSENBUG and G. F. MCCANN (*J. Biol. Chem.*, 1921, **47**, 529—539, 541—546).—The authors have confirmed the observations of Rona and Takahashi (A., 1911, ii, 302)

and of Cushny (A., 1920, i, 508) that 30—40% of the calcium in serum is non-diffusible; this percentage is not changed by altering the carbon dioxide saturation of the serum between 17 and 62 mm. Although, as Howland and Marriott (*Quart. J. Med.*, 1917, **11**, 289) have shown, there is a slight diminution in the calcium content of serum in rickets, the percentage of non-diffusible calcium here remains normal, and the same applies to the greater diminution in calcium during tetany, after removal of the parathyroids, as observed by MacCallum and Voegtlin (*J. exp. Med.*, 1909, **11**, 118). The method of analysis is by compensatory dialysis. G. B.

Animal Calorimetry. XVII. The Influence of Colloidal Iron on the Basal Metabolism. EINAR LANGFELDT (*J. Biol. Chem.*, 1921, **47**, 557—563).—Intravenous injection of negative ferric hydroxide sol (Fischer, A., 1910, ii, 856) in dogs increased the heat production by 7—15%, increased the oxygen consumption and carbon dioxide output, and slightly increased the respiratory quotient. The chief increase of the total heat production falls in the non-protein metabolism. G. B.

The Metabolism of Nitrobenzaldehydes and Nitrophenylacetaldehyde. CARL P. SHERWIN and WALTER A. HYNES (*J. Biol. Chem.*, 1921, **47**, 297—301).—After ingestion by man, *o*-, *m*-, and *p*-nitrobenzaldehydes and *p*-nitrophenylacetaldehyde were largely recovered from the urine in the form of the corresponding carboxylic acids. The *m*- and *p*-nitrobenzaldehydes were also, to some extent, excreted as nitrohippuric acid. In no case was reduction of the nitro-group observed. E. S.

Antiketogenesis. I. An *in vitro* Analogy. II. The Ketogenic–Antiketogenic Balance in Man. PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **47**, 433—448, 449—473).—Dextrose, lævulose, and glycerol (but not lactic acid) greatly increase the rate of oxidation of acetoacetic acid by hydrogen peroxide at room temperature. Evidently a chemical reaction occurs between some derivative of dextrose and acetoacetic acid, involving definite molecular quantities of each substance.

This "ketolytic" action *in vitro* is similar to the long-known "antiketogenic" action of carbohydrates in preventing the appearance of acetone substances in man. Using mainly experimental data of others, the author calculates the amount of acetoacetic acid which might be produced from the fatty acid and protein of various diets and finds that the minimum molecular ratio of ketogenic to antiketogenic substances for the avoidance of ketonuria (and β-hydroxybutyric acid) is unity. For a case of "total" diabetes with extreme acidosis, the author is enabled to calculate from the diet with fair accuracy the amount of β-hydroxybutyric acid actually excreted. G. B.

Chemical Examination of the Amniotic Fluid. R. CLOGNE and J. RÉGLADE (*Bull. Soc. Chim. Biol.*, 1921, **3**, 279—282).—The results are given of a number of estimations of urea in the amniotic fluid, and in the urine of new-born children. No parallelism between

the two is found, the concentration in the urine being much the higher. Examination of the amniotic fluid for ferments (oxydases and reductases) gave negative results. C. R. H.

Odoriferous Substances and the Sense of Smell. A. TSCHIRCH (*Schweiz. Apoth. Zeit.*, 1921, **59**, 229—232, 241—246, 254—258, 265—272; from *Chem. Zentr.*, 1921, iii, 190—191).—A theoretical discussion of the relationships between odour and chemical constitution and also of the mechanism of odour-perception. Whilst quality of odour cannot be correlated with chemical constitution, yet certain groups appear to be connected with intensity of odour. The odour of a substance depends on its solubility in air and also on its partition coefficient between air and the lipoid plasma of the olfactory cells. The sensation of smell is probably due to the formation of loose compounds of the odoriferous substance with the olfactory cell plasma and is thus a chemical stimulus. G. W. R.

Lipase. I. The Hydrolysis of the Esters of some Dicarboxylic Acids by the Lipase of the Liver. ADAM A. CHRISTMAN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, **47**, 495—505).—The lipase from pig's liver eliminates only one ethyl group from ethyl succinate and ethyl malonate. Ethyl hydrogen malonate was probably isolated. This and potassium ethyl malonate are not attacked by the lipase. G. B.

Effect of Hydrochloric Acid Ingestion on the Composition of the Urine in Man. RAYMOND L. STEHLE and ARTHUR C. MCCARTY (*J. Biol. Chem.*, 1921, **47**, 315—319).—The ingestion of hydrochloric acid causes an increased excretion of potassium, sodium, ammonia, phosphoric acid, and hydrogen ions in the urine. E. S.

Urobilin and Stercobilin [in the Urine] of Infants. MARCEL BRULÉ and H. GARBAN (*Compt. rend. Soc. Biol.*, 1921, **84**, 482—483; from *Chem. Zentr.*, 1921, iii, 184).—In the examination of urines, when urobilinogen is changed into urobilin the oxidation is generally carried too far, so that urobilin is decomposed. The authors recommend the addition to 10 c.c. of urine of a small quantity of zinc acetate and an equal volume of 95% alcohol. The liquid is filtered after half an hour and tested by means of fluorescence. Urine of newly-born infants, of high density, contains much urobilin; in urine of lower density urobilin is detected with difficulty. There is no correlation between the urobilin content of the urine and the appearance of stercobilin. Urobilin may be found considerably before stercobilin appears. Urobilin in the newly born is formed from the blood pigment and is due to hyperhæmolysis. These facts contradict the "enterohepatic" theory of urobilinuria. G. W. R.

Pyrrole and Melanuria. IV. P. SACCARDI (*Gazzetta*, 1921, **51**, ii, 108—112; cf. this vol., i, 203, 790).—2:5-Dimethylpyrrole has been examined by the author as a possible source of melanin. It is found that, *in vitro*, this compound does not yield melanogen, whereas, when introduced hypodermically into the animal

organism, it undergoes profound modification, being certainly demethylated and probably carboxylated by oxidation of the methyl groups; it seems likely that the pyrrole ring is connected by means of the carboxyl groups with the remainder of the melanogen molecule.

2 : 5-Dimethylpyrrole is readily ingested and is eliminated only very slowly, the urine becoming slightly melanotic. Enzymic oxidation *in vitro* is insufficient to transform it into melanogen or melanin. T. H. P.

The Degradation of *n*-Valeric Acid in the Animal Organism. L. Blum and E. Aubel (*Bull. Soc. Chim. Biol.*, 1921, **3**, 307—310).—The authors have isolated *d*-lactic acid and pyruvic acid from the urine of rabbits after intravenous injection of an aqueous solution of the sodium salt of *n*-valeric acid. C. R. H.

Pharmacology of Acridine and Acridinium Compounds. Emil Lenz (*Zeitsch. ges. exp. Med.*, **12**, 195—261; from *Chem. Zentr.*, 1921, iii, 188—189).—The pharmacology of the following compounds was investigated: 3 : 6-diaminoacridinium chloride; 3 : 6-diamino-10-methylacridinium chloride ('trypaflavine'); 3 : 6-diamino-2 : 7-dimethylacridine ('acridine-yellow'); 3 : 6-diamino-2 : 7 : 10-trimethylacridinium nitrate ('brilliant phosphine nitrate'); 3:6-diaminodimethyl-2:7:10-trimethylacridinium nitrate ('brilliant iminophosphine'); the silver double salt of trypaflavine ('argoflavine'); and 'septacrol' (additive product of silver nitrate and 'brilliant phosphine nitrate').

'Trypaflavin' in 0·005*N*-solution is immediately fatal to protozoa, and exerts an effect even in 0·00025*N*-solution. 'Brilliant iminophosphine' is somewhat stronger and 'acridine yellow' slightly weaker in effect. 'Trypaflavine' and 'brilliant iminophosphine' induce motor and respiratory paralysis, inhibition of reflexes, central paralysis, and finally cardiac failure in frogs. The lethal dose is 0·8—1 milligram per gram live weight in the case of 'trypaflavine' and 0·54 milligram in the case of 'brilliant iminophosphine.' With warm-blooded animals (mice, guinea pigs, and rabbits) these compounds are correspondingly poisonous.

The respiratory paralysis caused by large doses is consequent on central paralysis. One-third to one-half of the fatal dose causes transitory respiratory disturbances, whilst with somewhat larger doses a stage of excitement is reached. The circulation is affected when the respiratory paralysis is advanced. Other experiments showed that this effect was not secondary, but was due to a direct action on the vascular system. In frogs, the heart is a point of attack of the poison. Finally, peripheral vascular paralysis also occurs. In rabbits and guinea pigs local irritation of the cornea together with 'acridine leucocytosis' occurred. After lethal doses, all organs show a yellow coloration. The compounds are found in the urine immediately after intravenous or subcutaneous injection. Only traces of the poison are found in the spinal fluid. 'Brilliant iminophosphine' is more poisonous than 'trypaflavine.'

G. W. R.

Experimental Rickets in Rats. II. The Failure of Rats to develop Rickets on a Diet Deficient in Vitamin-*A*. A. F. HESS, G. F. MCCANN, and A. M. PAPPENHEIMER (*J. Biol. Chem.*, 1921, **47**, 395—409).—The authors do not confirm E. Mellanby's view, that the cause of rickets is a deficiency of the fat-soluble vitamin. G. B.

Experimental Rickets. VIII. Production of Rickets by Diets Low in Phosphorus and Fat-soluble-*A*. E. V. MCCOLLUM, NINA SIMMONDS, P. G. SHIPLEY, and E. A. PARK (*J. Biol. Chem.*, 1921, **47**, 507—527).—Rickets (in rats) is not simply due to a deficiency of vitamin-*A*, as suggested (for dogs) by E. Mellanby. To produce rickets, the calcium : phosphorus ratio of the diet must be upset, making its calcium content relatively high, its phosphorus content low. With a calcium : phosphorus ratio differing from the optimal for normal ossification, rickets may still be avoided by giving an antirachitic substance such as cod-liver oil. The ratio of calcium : phosphorus is of "infinitely greater importance" in ensuring normal ossification than the absolute amounts of these elements in the diet. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Pressure developed by Alcoholic Fermentation. R. KOLKWITZ (*Ber. Deut. bot. Ges.*, 1921, **39**, 219—223).—Although the viability of yeasts and other micro-organisms is not affected by pressures amounting to thousands of atmospheres and yeast-cells occur and vegetate normally in marine oozes under pressures of more than thirty atmospheres, the pressure developed by the evolution of carbon dioxide in alcoholic fermentation is generally estimated as little more than twelve atmospheres. Working with a specially constructed apparatus, the author was able to obtain a pressure of forty atmospheres by fermentation for three to five hours. The gradual slowing down of the evolution of carbon dioxide which was observed is attributed to narcosis by the dissolved gas rather than to the direct effect of the pressure produced. Microscopic examination showed that the older yeast-cells which had been exposed to high pressure had suffered injury by contraction of their protoplasmic contents. The younger cells appeared homogeneous. Placed in a fresh nutrient solution under normal pressure, fermentation took place relatively slowly at first. The experiments show that yeast fermentation is possible under relatively high pressures, and that it is not necessary to assume the existence of yeast organisms specially adapted to high pressures in the greater depths of the sea. G. W. R.

Production of Glycerol by Alcoholic Fermentation. K. SCHWEIZER (*Chim. et Ind.*, 1921, **6**, 149—159).—The author

discusses the mechanism of alcoholic fermentation of sugars and the formation of glycerol among the accessory products of the action. A summary is given of the methods by which the normal course of fermentation has been modified in order to produce glycerol. G. W. R.

Vitamin Content. II. The Yeast Test as a Measure of Vitamin-*B*. WALTER H. EDDY, HATTIE L. HEFT, HELEN C. STEVENSON, and RUTH JOHNSON (*J. Biol. Chem.*, 1921, **47**, 249—275).—Confirmatory evidence is produced showing that the yeast test is not a quantitative measure of vitamin-*B* content. It is possible, however, that the presence of vitamin-*B* is one of the factors causing the stimulation of the growth of yeast by vegetable extracts (cf. Fulmer, Nelson, and Sherwood, this vol., i, 292; Nelson, Ellis, Fulmer, and Cessna, *ibid.*, i, 386; MacDonald and McCollum, *ibid.*, i, 480). E. S.

Oligodynamy. Activation of Water by Copper and its Oxides. RAUL WERNICKE and ALFREDO SORDELLI (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 145—182).—The authors give a comprehensive review of previous work on the subject of oligodynamy. In order to determine whether the activation of water is due to solution of the activating substance, the behaviour of copper was studied. As a reagent for detecting the presence of copper at great dilutions, an aqueous solution containing *p*-phenylenediamine, α-naphthol, and sodium hydroxide was used. The bactericidal action of the waters obtained was tested on cultures of paratyphus-*A*. The results showed that activation was always accompanied by solution of copper, and that when no solution took place water was not activated. Activation was not produced in the case of water distilled in an atmosphere of oxygen or hydrogen. The presence of both oxygen and carbon dioxide would appear to be necessary for activation to take place. It was shown that water containing 1 : 3,000,000 of copper had a bactericidal action. The efficacy of such dilute solutions is explained by assuming colloidal adsorption of the dissolved substance by the organism. G. W. R.

The Rôle of Osmotic Pressure in the Toxicity of Soluble Salts. J. E. GREAVES and YEPPA LUND (*Soil Sci.*, 1921, **12**, 163—181).—The effect of chlorides, sulphates, carbonates, and nitrates of potassium, sodium, calcium, magnesium, iron, and manganese when added to soils in varying quantities, on the osmotic pressure and on ammonifying and nitrifying organisms was determined. With the exception of manganese nitrate, iron nitrate, and sodium carbonate there was a close correlation between toxicity and osmotic pressure. There is, however, probably also a physiological action of the salts in the living protoplasm such that it cannot function normally. W. G.

The Respiration of Leaves in a Vacuum or in Atmospheres Poor in Oxygen. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1921, **173**, 373—378).—The length of time during which

leaves will remain alive in the dark in atmospheres poor in oxygen depends on the absolute amount of oxygen present rather than its relative pressure. The small amount of oxygen, which results from the decomposition of the respiratory carbon dioxide by the chlorophyll function, in light, is sufficient for the leaf during the night. Normal respiration is absolutely essential for the maintenance of plant life. Intracellular and normal respiration proceed from different causes, and must be regarded as autonomous functions, as much by their intimate mechanism as by their influence on the life of green plants. W. G.

Composition of Gases in the Intercellular Spaces of Apples and Potatoes. J. R. MAGNESS (*Bot. Gaz.*, 1920, **70**, 308—316; from *Chem. Zentr.*, 1921, iii, 175).—With rise of temperature the amount of carbon dioxide increases, whilst the amount of oxygen decreases to a smaller extent. G. W. R.

The Resistance of Plants to Asphyxia. L. MAQUENNE and E. DEMOUSSY (*Bull. Soc. Chim. Biol.*, 1921, **3**, 273—278).—Germination can follow a normal course in seeds which are immersed in water, provided that the latter contains dissolved oxygen. Green leaves will survive for a considerable period in circulating water, and in stagnant water if exposed to sunlight; they will also live for several days in a vacuum tube, if exposed to the sun during the daytime. C. R. H.

The General Presence of Manganese in the Vegetable Kingdom. GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1921, **173**, 333—336).—It is shown that the various plants and parts of plants which Maumené reported as devoid of manganese (cf. *Compt. rend.*, 1884, **98**, 1416) do without exception contain manganese. Thus the presence of manganese is general in all the organs and species of the vegetable kingdom. W. G.

The Distribution of Iron in Plants. L. MAQUENNE and R. CERIGHELLI (*Compt. rend.*, 1921, **173**, 273—278).—Iron enters only to a comparatively slight extent into the composition of plant tissues. In general its distribution in plants is comparable with that of copper (compare Maquenne and Demoussy, A., 1920, i, 270), the young organs, buds or leaves, containing more than the old ones. Like copper, it is capable of migrating in plant tissues, tending to move towards the centres of active life and reproduction. W. G.

Extraction and Nature of the Hydrosulphide Compound in the Seeds of certain *Papilionaceæ*. MARCEL MIRANDE (*Compt. rend.*, 1921, **173**, 252—253).—The substance present in the seeds of *Lathyrus* and other *Papilionaceæ*, which by autofermentation in contact with water gives rise spontaneously to hydrogen sulphide, is apparently a protein which thus loses the labile sulphur which it contains. W. G.

Constituents of the Root of Gishi-gishi. YOSHIHARU MURAYAMA and TAKEKI ITAGAKI (*J. Pharm. Soc. Japan*, 1921, 327—330).—From a hot alcoholic extract of the dried root of gishi-gishi (*Rumex crispus*, L. var. *japonicus*, Makino), the authors isolated 0·12% of frangula-emodin, $C_{15}H_{10}O_5$, orange-red prisms, m. p. 250—252°, and 0·5% of chrysophanic acid, this being partly free in the extract and partly combined with sugar.

K. K.

The Existence of Anthocyanidins in the Free State in the Fruits of *Ruscus aculeatus* and *Solanum Dulcamara*. ST. JONESCO (*Compt. rend.*, 1921, **173**, 168—171).—Anthocyanidins exist in the free state in the fruits of *Ruscus aculeatus* and *Solanum Dulcamara*, picked in July before they were fully ripe. They are found along with anthocyanins in the red pigment which gives the colour to the fruit.

W. G.

Japanese Birdlime. HIDEKICHI YANAGISAWA (*J. Pharm. Soc. Japan*, 1921, No. **471**, 405—423).—Japanese birdlime is of two kinds. The best, which is red, is made from the bark of *Trochodendron aralioide*, whilst the white one (common kind) is prepared from many kinds of *Ilex* and related plants (cf. *Bot. Mag.*, **28**, Nos. 229 and 230). By the saponification of the red variety with alcoholic potash, palmitic acid, resin, and a neutral unsaponifiable crystalline substance, *trochol*, were isolated. A caoutchouc, a slightly brown mass, which gave a bromine additive compound,

$$C_{10}H_{15}(HBr)Br_4,$$

was also obtained. After purification by precipitation from chloroform solution by light petroleum and recrystallisation from chloroform–alcohol, trochol forms colourless needles or prisms,

$$C_{26}H_{44}O_2,\tfrac{1}{2}(C_2H_6O+H_2O),$$

m. p. 252°, $[\alpha]_D^{15}$ +20° (in chloroform–alcohol). It yields a *diacetate*, colourless needles or prisms, m. p. 217°, from which by treatment with bromine, a bromo-derivative, $C_{26}H_{40}Br_2(OAc)_2$, m. p. 293°, was obtained although trochol itself gave no definite bromine compound. The *dibenzoate* of trochol forms colourless needles, m. p. 172° (sintering at 145°); the *monobenzoate* forms colourless leaves, m. p. 282°. Trochol seems to occur as the palmitic ester in the birdlime, and by heating the two components at 200° in a vacuum, the ester was produced as a colourless, viscous substance. *Trochol cinnamate* was prepared by the same method as yellow, lustrous crystals, m. p. 155°, after sintering at 132°.

From the white birdlime, by saponification with alcoholic potash, an alcohol, $C_{26}H_{45}OH$, m. p. 222°, was prepared, which gave an acetate, m. p. 203°. All the properties of the alcohol correspond with the mochyl alcohol of Divers and Kawakita (T., 1888, **53**, 268).

K. K.

Organic Chemistry.

Preparation of Ethylene by Hydrogenation of Acetylene. WILLIAM H. ROSS, JAMES B. CULBERTSON, and J. P. PARSONS (*J. Ind. Eng. Chem.*, 1921, **13**, 775—778).—Metallic nickel, prepared by reducing the oxide at 300°, has a greater capacity than has coconut charcoal for adsorbing hydrogen at the ordinary temperature. When a mixture of equal volumes of hydrogen and acetylene is passed into a tube, from which the air is exhausted, about one-third filled with freshly-reduced nickel, the hydrogen adsorbed by the nickel, together with that added, may be sufficient to convert the acetylene completely into ethane. If the tube is then exhausted and the mixture of hydrogen and acetylene introduced until the excess of hydrogen is used up, a product may be obtained which contains more than 80% of ethylene. The best results are obtained when the mixture contains a slight excess of hydrogen, but as this is further increased, the amount of ethylene decreases and the quantity of ethane increases correspondingly. The adsorbed hydrogen in an active nickel catalyst may be eliminated by repeated treatment with acetylene; whilst the nickel does not lose its activity, it is then without action on either ethylene or acetylene. W. P. S.

Unsaturation and Molecular Compound Formation. II. O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1921, **43**, 1227—1230; cf. A., 1918, i, 534).—Freezing-point determinations have been made for the system allylene–hydrogen bromide, and from these it is shown that two eutectics and one molecular compounds exist. The eutectics lie at −132° and −138° respectively, and the molecular compound, C_3H_4,HBr, melts at −126°. The behaviour of allylene in forming a molecular compound differs from that of acetylene, but this difference is the same as was observed in the case of benzene and substituted benzenes, and confirms the authors' view that the formation of an atomic compound is always preceded by the formation of a molecular compound (*loc. cit.*). Exact details are given of a method, based on that of Lebeau and Pichon (A., 1913, i, 438), for the preparation of large quantities of pure allylene. The pure substance melts at −105·0° and boils at −27·0°. Under ideal conditions, the value 40 is found for the molecular weight. J. F. S.

Molecular Rearrangement of Unsaturated Compounds in Acid Solution. ALF. GILLET (*Bull. Soc. chim. Belg.*, 1921, **30**, 226—252).—The general rules already enunciated (this vol., i, 533) are illustrated by numerous examples. The opening of a tri-methylene ring by addition of water or acids conforms with the rules referred to. Examples of the converse reaction are lacking, but the compound CH_2:CMe·CMe:CH_2, which is the "normal" product of dehydration of pinacone, may be expected, owing to the negative

character of the CH_2 groups and the positive character of the intermediate groups, to undergo transformation into the following compounds in acid solutions : $CH_2<\genfrac{}{}{0pt}{}{CMe}{CMe}>CH_2 \longrightarrow OH\cdot CMe<\genfrac{}{}{0pt}{}{CMe_2}{CH_2}$ $\longrightarrow$ $O\colon CMe\cdot CMe_3$ (pinacolin). This explains the mechanism of the various transformations undergone by the pinacones and analogous compounds, numerous examples of which are cited and classified. The various types of "ethylenic transformations" (*loc. cit.*), such as shifting of the double bond, addition or subtraction of water or acids, and keto-enol rearrangements, and the mechanism of the dehydration of alcohols, are discussed from the point of view of the general rules. Many of these cases are explained very simply, but for others the intermediate formation and rupture of one or two trimethylene rings is assumed. The type of transformation in any case depends chiefly on the constitution of the compound and the electro-positive or -negative character of the radicles present. The catalyst as a rule plays a very subordinate part in determining the character of the reaction. J. H. L.

Preparation of Alkyl Vinyl Ethers and their Homologues. PLAUSONS FORSCHUNGSINSTITUT G. M. B. H. (D.R.-P. 338281; from *Chem. Zentr.*, 1921, iv, 421. See also Plauson and Vielle, Brit. Pat. 156121).—Homologues of alkyl vinyl ethers are prepared by replacement of the C_2H_2 group by homologous groups. *Ethyl vinyl ether*, b. p. 35°/760 mm., is decomposed by sulphuric acid. G. W. R.

The Molecular Conductivity of some Sulphonium Compounds in Acetone. SIR PRAPHULLA CHANDRA RÂY and KALIKUMAR KUMAR (T., 1921, **119**, 1643—1644).

Decomposition of Ethyl Thioacetate by Mercury Salts; a Contribution to the Chemistry of Mercury Mercaptides. GEORG SACHS (*Ber.*, 1921, **54**, [*B*], 1849—1854).—Ethyl thioacetate is remarkably resistant towards solutions of alkali hydroxide by which it is hydrolysed slowly to ethyl mercaptan and acetic acid. It is therefore remarkable that a similar hydrolysis is immediately induced by the addition of an alcoholic solution of mercury acetate to the ester, ethylmercaptomercurichloride, $SEt\cdot HgCl$, being precipitated by the addition of water and sodium chloride to the product. It appears necessary in some degree to use the mercury compound in the form of its acetate, since only a slow hydrolysis is observed with mercuric chloride solution, and it is suggested that the compound $SEt\cdot Hg\cdot OAc$ is initially formed and remains in solution. Evidence in favour of this hypothesis is adduced from the formation of the compound $C_4H_8O_2SHg$, microscopic rods, m. p. 140—146°, when solutions of ethyl thioacetate and mercuric acetate in acetic anhydride are mixed; by a modification of the conditions of this reaction it is found possible to isolate a second *compound*, $C_{12}H_{22}O_8S_2Hg_3$, m. p. 140—142°, to a turbid liquid, decomp. 144—146°, which is also produced from mercuric acetate and ethyl mercaptan in acetic anhydride solution. Prolonged agitation of

ethylmercaptomercurichloride with a saturated ethereal solution of mercuric chloride leads to the formation of the additive *compound*, $SEt\cdot HgCl,HgCl_2$, slender needles or prisms, m. p. 150° (decomp.).

H. W.

Experiments on the Synthesis of the Polyacetic Acids of Methane. III. Conditions Controlling Synthesis by the Cyanoacetic Ester Method—(*continued*). CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN (T., 1921, **119**, 1582—1601).

Solubilities of some Active and Racemic Tartrates and Malates. MARCEL DUBOUX and LÉON CUTTAT (*Helv. Chim. Acta*, 1921, **4**, 735—761).—A series of determinations carried out with the object of ascertaining whether the salts of inactive acids are invariably less soluble than those of the active forms. Of the compounds investigated, barium tartrate is the only exception to this rule. Analytical applications of this are referred to (Kling, A., 1910, ii, 359; Duboux, *Bull. Soc. Vaud. Sci. Nat.*, 1916, **51**, 55), and it is mentioned that calcium is better estimated in water as racemate than as oxalate, since magnesium does not then affect the results (Caeiro, *Diss.*, Lausanne, 1918).

The values given are in terms of grams of anhydrous salt per 100 grams of solution at temperatures of 0°, 12·5°, 25°, and 37·5°.

Tartrates. *Active.*—$MgA,4H_2O$, 0·540, 0·848, 1·174, 1·050; $CaA,4H_2O$, 0·0192, 0·0268, 0·0360, 0·0498; $SrA,4H_2O$, 0·0942, 0·1285, 0·1765, 0·2395; $BaA,\frac{1}{2}H_2O$, 0·0200, 0·0247, 0·0294, 0·0341; PbA, 0·0027, 0·0030, 0·0035, 0·0046.

Inactive.—$Mg_2A_2,10H_2O$, 0·403, 0·582, 0·826, 1·095; $Ca_2A_2,8H_2O$, 0·0023, 0·0034, 0·0045, 0·0056; $Sr_2A_2,8H_2O$, 0·0107, 0·0202, 0·0297, 0·0392; Ba_2A_2, 0·0243, 0·0284, 0·0325, 0·0366; $Pb_2A_2,4H_2O$, 0·0038, 0·0020, 0·0034, 0·0066.

Malates. *Active.*—$MgA,3H_2O$, 2·02, 2·28, 2·54, 2·80; $CaA,2H_2O$, 0·670, 0·805, 0·921, 1·011; $SrA,4H_2O$, 0·193, 0·332, 0·490, 0·781; BaA, 1·020, 1·150, 1·240, 1·310, $PbA,2H_2O$, 0·015, 0·027, 0·052, 0·089.

Inactive.—$Mg_2A_2,5H_2O$, 0·93, 1·08, 1·23, 1·38; $Ca_2A_2,3H_2O$, 0·244, 0·277, 0·310, 0·343; $Sr_2A_2,5H_2O$, 0·290, 0·325, 0·422, 0·550; Ba_2A_2,H_2O, 0·76, —, 0·58, 0·84; $Pb_2A_2,2H_2O$, 0·015, 0·023, 0·035, 0·0545.

Above 26·2°, active magnesium tartrate is dihydrated. J. K.

Ethylglycoloside as a Type of αβ-Glucosides. MAX BERGMANN and ARTUR MIEKELEY (*Ber.*, 1921, **54**, [*B*], 2150—2157).—The discovery of γ-methylglucoside, the behaviour of the rhamnosides, and the attribution of an ethylene oxide structure to the glucosidic oxygen bridge in lævulose, inulin, etc. (cf. Haworth and Law, T., 1916, **109**, 1324; Irvine and Steele, T., 1920, **107**, 1474), has increased the interest in this type of substance, and the authors have therefore prepared ethylglycoloside, $\begin{matrix}CH_2\\|\\O\end{matrix}\!\!>CH\cdot OEt$, as a very simple member of the series. When dissolved in phenol at 30—40°, the substance

is bimolecular, but unimolecular under greatly diminished pressure at 160°; the hypothesis that the action is of the type, $\underset{O}{\overset{CH_2}{|}}\!\!>CH\cdot OEt \rightleftharpoons \begin{matrix} CH_2\cdot CH(OEt)\cdot O \\ | \qquad\qquad\qquad | \\ O-CH(OEt)-CH_2 \end{matrix}$, analogous to that assumed in the case of glycollaldehyde appears to be highly improbable. Its close relationship to ethylene oxide renders it less stable than the usual α- and β-glucosides; it is scarcely affected by water, and hence does not reduce Fehling's solution, even at the boiling point, but, on the other hand, it is exceedingly sensitive to acids, being rapidly hydrolysed to a certain extent by boiling *N*/1000-hydrochloric acid. When treated with phenylhydrazine hydrochloride and sodium acetate, it gives a somewhat considerable amount of glyoxalosazone, the effect being due to the presence of free acetic acid. This property is shared by other non-furoid glucosides, for example γ-methylrhamnoside. In this connexion, it is pointed out that sucrose is not so indifferent towards the phenylhydrazine mixture as is generally supposed. In general, the osazone test does not seem well adapted in every case for distinguishing between glucoside and free sugar.

Ethylglycoloside, m. p. 59—60°, after softening at 58°, b. p. 90°/12 mm., 122°/51 mm., is prepared by the action of perbenzoic acid on a well-cooled solution of ethyl vinyl ether in absolute ether; it has $d_4^{21\cdot5}$ 1·0436, d_4^{24} 1·0428, n_D^{20} 1·4293. It is converted by an alcoholic solution of hydrogen chloride into glycollaldehyde acetal.

The authors proposed to designate glucosides of known structure by adding to their names two figures denoting the points of attachment of the glucosidic oxygen bridge, the enumeration, as in the case of dextrose, to commence with the aldehydic carbon atom, for example, methylglucoside-(αδ), ethylglycoloside-(αβ); ε-glucosido-(αδ)-mannose. H. W.

Mytilitol, a Naturally Occurring Cyclose. D. Ackermann (*Ber.*, 1921, **54**, [*B*], 1938—1943).—The isolation of mytilitol from *Mytilus edulis* is described in detail. It forms colourless, lustrous crystals, m. p. 259°, is optically inactive, and does not contain a methoxyl group. It is converted by acetic anhydride into a *penta-acetate*, microscopic needles, m. p. 157—158°, and by acetic anhydride and concentrated sulphuric acid into the *hexa-acetate*, m. p. 180—181°. The parent substance is therefore regarded as methyl*cyclo*hexanehexol. It has been examined previously by Jansen (A., 1913, i, 791), who regarded it as *cyclo*hexanepentol. It is difficult to decide between the two conceptions on the basis of analyses of the parent substance and of its derivatives, but the percentage of water of crystallisation in hydrated mytilitol and the values for carbon in the anhydrous substance harmonise better with the present formula, which is further supported by the insolubility of mytilitol in organic solvents and its sparing solubility in cold water; it is scarcely conceivable that an isomeride of quercitol would exhibit these properties. H. W.

Optical Rotation of Dextrose under the Influence of Hydrochloric Acid. II. The Change of Rotatory Power and Reducing Capacity of Dextrose Solutions in Hydrochloric Acid at 100°. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1921, **116**, 171—190; cf. A., 1920, i, 661).—The optical activity and reducing capacity of 20, 10, 5, and $2\frac{1}{2}$% dextrose solutions in 5·1, 8·1, and 10·1% hydrochloric acid solutions were determined over a period of twelve hours at 100°. In general, the behaviour of both properties in the first two hours shows considerable variation, but afterwards the fall in rotation and reducing power is a linear function of the time, and the greater the concentration of the acid the greater the effect produced. For 10 and 20% dextrose solutions, a maximum of optical rotation is attained in the first two hours, due, probably, to the formation of *iso*maltose. H. K.

Polysaccharides. X. Anhydro-sugars of the Trehalose Type: Diglucan and *iso*Diglucan. P. KARRER, FR. WIDMER, and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, **4**, 796—801).—By the action of silver carbonate on a suspension of acetodibromoglucose in chloroform, ζ-bromo-$\beta\gamma\epsilon$-triacetylglucose is produced, with a small proportion of two forms of $\zeta\zeta'$-dibromo-$\beta\gamma\epsilon\beta'\gamma'\epsilon'$-hexacetyl-$\alpha$-glucosidoglucose (I), neither of which reduces Fehling's solution until hydrolysed by acid.

$$\left[\begin{array}{l} CH_2Br\cdot CH(OAc)\cdot \underline{CH\cdot CH(OAc)\cdot CH(OAc)\cdot CH} \\ \qquad\qquad\qquad\qquad\qquad\qquad O \end{array}\right]_2 O.$$

(I.)

The *α-form*, m. p. 212°, is optically inactive and much less soluble in alcohol than the β-form, needles, m. p. 152°, $[\alpha]_D$ $-10{\cdot}2°$. The exact relationship of these compounds to the trehaloses remains undecided. Both are converted by boiling barium hydroxide solution into dianhydrodisaccharides, $C_{12}H_{18}O_9$. *Diglucan*, from the α-form, hexagonal polyhedra, m. p. 170—175°, $[\alpha]_D^{17}$ $-214{\cdot}1°$, is easily soluble in water. iso*Diglucan*, from the β-form, has not been crystallised, is lævorotatory, more readily soluble than diglucan in alcohol, and, like this, only reduces Fehling's solution after hydrolysis. They differ by the configurations of the asterisked carbon atoms in the formula

$$\left[\begin{array}{l} \qquad\qquad\qquad\qquad O \\ CH_2\cdot CH(OH)\cdot \overline{CH\cdot CH\cdot CH(OH)\cdot \overset{*}{C}H}- \\ \underline{\qquad\quad O \qquad\quad} \end{array}\right]_2 O$$

J. K.

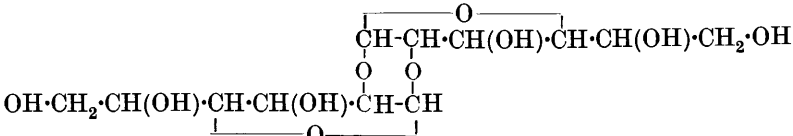
Polysaccharides. XI. Compounds of Anhydro-sugars with Alkali Hydroxides. A Method of Determining the Parent Compound of Polymeric Anhydro-sugars. P. KARRER (*Helv. Chim. Acta*, 1921, **4**, 811—820).—Solutions of di-, α-tetra-, β-hexa-, and α-octa-amyloses in dilute aqueous sodium hydroxide contain additive compounds, which are precipitated by alcohol, and after purification by solution and reprecipitation, respectively correspond exactly with the formulæ $C_{12}H_{20}O_{10}$,NaOH, $(C_{12}H_{20}O_{10},NaOH)_2$, $(C_{12}H_{20}O_{10},NaOH)_3$, and $(C_{12}H_{20}O_{10},NaOH)_4$.

Polymeric anhydro-sugars, as internal acetals, therefore combine with one molecule of sodium hydroxide per molecule of anhydro-sugar, and so permit the determination of the molecular weight of this. Thus β-hexa-amylose is a polymeric maltose anhydride (cf. this vol., i, 768), inulin is probably derived from anhydro-difructose (cf. Pfeiffer and Tollens, A., 1882, 490), and xylan from anhydro-dixylose (cf. Abderhalden, *Biochem. Handlex.*, ii, 32). In further confirmation of previous results, a *compound*, $(C_{12}H_{20}O_{10},NaOH)_x$, was obtained from soluble starch. It is suggested that such poly-saccharides are crystalline substances, of which the lattice points are occupied by polymeric molecules, which in the case of starch are diamylose complexes, $(C_{12}H_{20}O_{10})_2$ or $(C_{12}H_{20}O_{10})_3$. The forces of valency by which the polymeric molecules are fixed in the crystal are so strong that the resulting "crystal-polymerisation" very closely resembles true polymerisation. If the forces in question approximate in strength to those responsible for the existence of the polymerides, and also to those operating in the anhydro-sugar, it will be extremely difficult to isolate intermediate degradation products. This is probably the case with cellulose. J. K.

A New Method for the Preparation of Anhydro-sugars. P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, **4**, 817—820).—Acetobromoglucose combines with trimethylamine in alcoholic solution to form *tetracetylglucosidotrimethylammonium bromide*, $C_{17}H_{28}O_9NBr$, well-defined polyhedra of neutral reaction, m. p. 192°, $[\alpha]_D^{18}+10{\cdot}2°$, which is quantitatively converted into lævoglucosan by warming its aqueous solution for a short time with an alkali or alkaline earth hydroxide. Since this reaction is a form of the Hofmann degradation of quaternary ammonium hydroxides, and yet, if the current formula for lævoglucosan be accepted, results in ring formation, it is suggested that caution is necessary in deriving constitutional formulæ from such reactions. J. K.

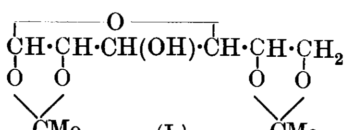
Polymerisation of Glucosan. AMÉ PICTET and JACQUES PICTET (*Helv. Chim. Acta*, 1921, **4**, 788—795).—Glucosan, like lævoglucosan (A., 1899, i, 527), may be polymerised by means of platinum black, but the change in each case is more conveniently effected with the aid of a trace of anhydrous zinc chloride. The product obtained from glucosan varies with the conditions employed. *Diglucosan*, $(C_6H_{10}O_5)_2$, m. p. 160° (decomp.), $[\alpha]_D$ $+54{\cdot}5°$ (*tetrabenzoate*, $C_{40}H_{36}O_{14}$, m. p. 128—129°), is produced at 155°/15 mm., is easily soluble in water, has a sweet taste, does not react with phenylhydrazine, and is hydrolysed by mineral and oxalic acids, but not by water. This is expressed by the formula (I). *Tetraglucosan*, $(C_6H_{10}O_5)_4,2H_2O$, $[\alpha]_D+82{\cdot}76°$ (*octa-acetate*, $C_{40}H_{58}O_{28}$, m. p. 84—85°; *octabenzoate*, $C_{80}H_{72}O_{28}$, m. p. 109—110°), is not completely dehydrated at 110°, and resembles the dextrins, especially those derived from lævoglucosan, in properties. It does not react with phenylhydrazine, but does so very slightly with Fehling's solution after prolonged boiling. Its mode of formation is probably similar to that of diglucosan,

and it is also produced from dextrose and zinc chloride at 180° under ordinary pressure. Tetralævoglucosan, from lævoglucosan and zinc chloride at 155°, appears to be to some extent depolymerised to lævoglucosan by distillation under reduced pressure. The rotatory power ($[\alpha]_D + 73 \cdot 85$) and molecular weight of the product of polymerisation of equal proportions of glucosan and lævoglucosan at 155° under ordinary pressure suggests the presence of a mixed polymeride, $(C_6H_{10}O_5)_4$, with those derived from the separate substances. No definite results were obtained from attempts by hydrolysis of these polymerides to secure partial degradation to disaccharides.



(I.) J. K.

Constitution of the Sugar-acetones. P. KARRER and O. HURWITZ (*Helv. Chim. Acta,* 1921, **4**, 728—734).—Glycerolacetone is attacked by alkaline permanganate at 20°, but glucose- and fructose-diacetones are almost quantitatively recovered after prolonged warming with this reagent. It is therefore concluded that both the terminal carbon atoms of the sugars are in each case involved in the condensation with acetone, the secondary alcoholic groups being sterically protected from oxidation. Similarly, lævoglucosan is almost unattacked (Vongerichten and Müller, A., 1906, i, 198; Pictet and Cramer, A., 1920, i, 819), whilst glucosan and lævulosan suffer immediate oxidation (cf. this vol., i, 544). The formula (I) is therefore proposed in preference to that of Irvine and Scott (T., 1909, **95**, 1220) for glucosediacetone, and equally explains its reactions (Irvine and Scott, *loc. cit.*; Irvine and Paterson, T., 1914, **105**, 908). Fructosediacetone is written (II), the mode of attachment of the bridge oxygen atom explaining the identity of the osazones from the monomethyl-glucose and -fructose respectively obtained from glucose- and fructose-diacetones (Irvine and Scott, *loc. cit.*). Irvine and Paterson's formula for α-mannitoldiacetone, with a primary alcoholic group, is confirmed, whilst the β-isomeride (Fischer and Rund, A., 1916, i, 863) is only slightly attacked, although the fact that it contains two free hydroxyl groups as compared with one in the cases of glucose- and fructose-diacetones renders it less resistant. It is assigned the formula (III).



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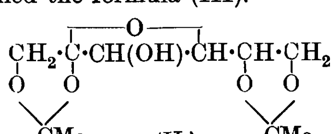

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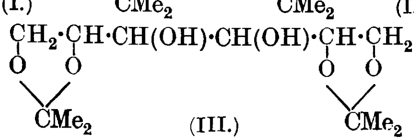


(III.) J. K.

Starch. A. Reychler (*Bull. Soc. chim. Belg.*, 1921, **30**, 223—226; cf. this vol., i, 498).—Modifying an experiment described by Roux (A., 1905, i, 262), the author has isolated a reversion product from starch paste, after prolonged chilling. It is concluded that the reversion process concerns chiefly the parietal matter of the starch grain, and that this matter is very similar to the "artificial starch" or the "amylose" of Maquenne. The author reaffirms his earlier statement that each starch grain possesses two hila, one on each side of the grain. J. H. L.

Starch. A. Reychler (*Bull. Soc. chim.*, 1921, [iv], **29**, 833—836; cf. this vol., i, 498).—As a result of further experimental work, the author concludes that the starch grain has a protective coating, which is very little acted on by cold water. It swells up, is distended, and more or less ruptured by boiling water. In a fresh starch paste, this material is easily liquefied by malt extracts, but if it has been kept for some days it is more refractory. It then resists the action of diastase and maintains its characteristic form, finally giving a deposit, in the form of a gel, which cannot be saccharified. It is soluble when heated with water at 140—150° under pressure, but on cooling the solution, it is deposited again in the form of artificial starch or Maquenne's pure amylose (cf. A., 1906, i, 327, 547). W. G.

Polysaccharides. VIII. Starch and the Amyloses. P. Karrer, C. Nägeli, O. Hurwitz, and A. Wälti (*Helv. Chim. Acta*, 1921, **4**, 678—699; cf. this vol., i, 397).—α-Tetra-amylose does not yield acetobromomaltose when treated with acetyl bromide in entire absence of water, but an amorphous product containing bromine, and resembling that obtained from starch under similar conditions. The least trace of acetic acid induces the formation of the same proportion of acetobromomaltose as is obtained from an equal weight of maltose, a small amount of acetobromoglucose being also produced if the temperature be not maintained sufficiently low, for example below 10° for a trace of acetic acid. Air-dried soluble starch furnishes the same weight of acetobromomaltose as an equal quantity of maltose. Hence starch is a polymeride of anhydromaltose in which the glucose residues are not united by "glucoside-linkings." Further, acetylated starch, like acetylated triamylose, does not furnish bromo-compounds when treated with acetyl bromide, so that the opening of the anhydro-rings of starch by this reagent is due to hydrobromic acid. From dry β-hexa-amylose, however, a product is obtained very similar to, if not identical with, that derived from starch, whilst in presence of acetic acid the same proportion of acetobromomaltose is produced as from maltose. Hence β-hexa-amylose represents a polymeric form of maltose anhydride, isomeric with the α-amyloses.

Cold concentrated aqueous solutions of tetra-amylose give a blue colour with iodine, which disappears on warming, but reappears on cooling, like that of starch, but differs from this in that it is produced only in concentrated solution. Octa-amylose gives blue needles of an additive product, which is similarly affected by heat.

The α-amyloses, like starch, are converted into lævoglucosan by distillation in a vacuum, and also furnish potassium and sodium salts (cf. Pfeiffer and Tollens, A., 1882, 490). Octa- and β-hexa-amyloses are easily soluble in dilute sodium hydroxide solution.

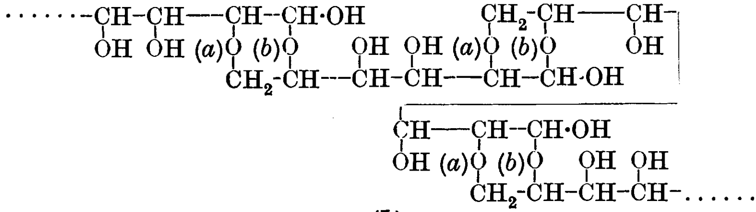
A further analogy between starch and the amyloses follows from their behaviour towards pancreas-diastase, which ferments di- and α-tetra-amylose to maltose to the extent of 10% (cf. Pringsheim, A., 1913, i, 1281), although β-hexa- and α-octa-amyloses are unaffected. Intestinal ferments of the snail do not attack α-tetra-amylose or methylated starches. Lævoglucosan furnishes acetobromoglucose when treated with a solution of hydrogen bromide in glacial acetic acid, owing to acetylation of hydroxyl groups produced by breaking down of the anhydro-oxygen linking. Hence the position of this in the α-amyloses cannot be determined by subjecting them to this reaction (this vol., i, 313).

The respective heats of combustion of 1 gram of anhydrous maltose, diamylose, α-tetra-amylose, β-hexa-amylose, α-octa-amylose, starch, and lævoglucosan are 3949, 4235, 4186, 4165, 4610, 4183, and 4186 calories. Hence α-octa-amylose, which has a larger heat of combustion than any other known carbohydrate, and so is produced during fermentation of starch by *Bacillus macerans* in greater quantity at 47° than at 32°, probably represents the most highly polymerised form of α-amylose possible. Further, starch itself cannot be more highly polymerised, and so is doubtless a member of a series of polymerisation products of maltose anhydride isomeric with the α-amyloses, and corresponding probably with α-tetra-amylose, $(C_{12}H_{20}O_{10})_2$, or β-hexa-amylose, $(C_{12}H_{20}O_{10})_3$. Although no direct proof of this can yet be supplied, it agrees with molecular-weight determinations of methylo-starches (this vol., i, 311) and of soluble starch (Beckmann and Maxim, A., 1915, ii, 222) and with the fact that, like those of starch (Lintner, A., 1888, 497; Asboth, A., 1887, 868) solutions of octa-amylose, and, in presence of alcohol, of β-hexa- and α-tetra-amyloses yield precipitates with barium hydroxide. The composition of these varies somewhat with circumstances, although those from natural and soluble starches agree fairly closely in composition with those obtained from α-tetra- and β-hexa-amyloses under similar conditions. Further, the heat of combustion of starch exceeds 4163 calories, which is calculated as the maximum possible for a compound composed of a continuous chain of glucose residues, but agrees closely with the values for the anhydro-sugars lævoglucosan and α-tetra-amylose. The fact that the same applies to cellulose (4180 calories) is considered as evidence that this also has an anhydro-formula. Methylated wheat starch (M 1060), rice starch (M 844), and maize starch are described. J. K.

The Constitution of Cellulose and Cellobiose. Astrid Cleve von Euler (*Chem. Zeit.*, 1921, **45**, 977—978, 998).—The important facts which must be taken into account in any structural formula assigned to cellulose are outlined and the directions in which all structural formulæ hitherto proposed for cellulose are

ff*

unsatisfactory are indicated. It is possible, however, to conceive a formula for cellulose which is in agreement with its constitution as a high molecular condensation product, and may be reconciled with the properties of its derivatives and fission products. Two variations of a new formula for cellulose are proposed which contain the *p*-dioxan ring of Green's formula (A., 1905, i, 22), but have the advantage over the latter that they contain a chain of hexose molecules of any desired length, thus :



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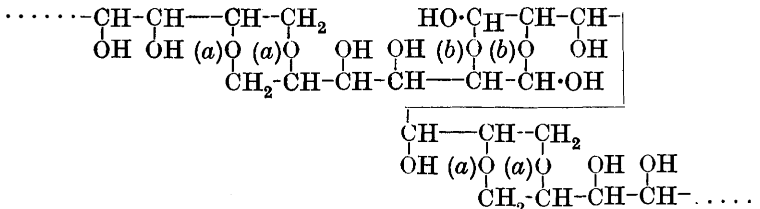


(II.)

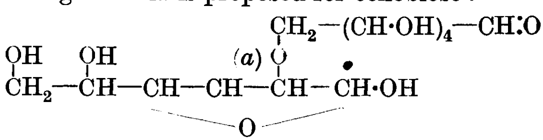
The connecting oxygen atoms are of two kinds and are distinguished in the formulæ as (*a*) and (*b*). The combination (*a*) represents an ordinary anhydride (ether) linking which on the addition of the elements of water reacts thus :

$$\vdots CH\cdot O\cdot CH_2 + H_2O = \vdots CH\cdot OH + \cdot CH_2\cdot OH.$$

In combination (*b*), on the other hand, the oxygen is in a semi-acetal combination, and fission of the linking is accompanied by activation of the carbonyl oxygen without alteration in the gross formula. The elements of water are added first and then removed from the intermediate carbonyl hydrate, so that the nett result is :

$$\vdots CH\cdot O\cdot CH\cdot OH \longrightarrow \vdots CH\cdot OH + \cdot CH\vdots O$$

Arguments are adduced in favour of these formulæ for cellulose and the following formula is proposed for cellobiose :



The author was unaware of the work of Haworth and Leitch (T., 1919, **115**, 813) on the latter subject when this paper was written. Apart from the fact that in the latter authors' formula for cellobiose both carbonyl groups are in acetal combination, the

two formulæ for cellobiose differ only in that the residues are united by an (*a*) combination in the case of von Euler, and a (*b*) combination in the case of Haworth and Leitch. A decision on this point could not be arrived at from a trimethylglucose prepared from methylated cellulose, as the fission would occur at the (*b*) combination in von Euler's cellulose formula in the preparation of cellobiose, but this point could be settled by the examination of the methylglucoside obtained from methylated cellobiose.

F. M. R.

Hydrolysis of Cellulose. YRJÖ KAUKO (*Naturwiss.*, 1921, **9**, 237—238; from *Chem. Zentr.*, 1921, iii, 526).—By saturating moist cellulose with hydrogen chloride in the cold, a thick solution is obtained which remains almost colourless even after forty hours. The solution thus obtained reacts with Fehling's solution to the extent of 40—60% of the theoretical amount of dextrose, if complete transformation were assumed. With increasing time of reaction, increasing amounts of substances giving dextrose after autoclaving are formed. As much as 90% of dextrose may be obtained if sufficient time be allowed for the reaction. At 13°, 80% is obtained within four hours. Above this temperature, dark coloured products are obtained. The yield of dextrose is markedly increased by moistening the cellulose with larger quantities of water. A quantitative method for the estimation of cellulose might be developed, using this reaction. G. W. R.

Nature of the Swelling Process. V. Swelling and Partition in the System Nitrobenzene-Alcohol-Cellulose Acetate. E. KNOEVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, **14**, 1—24; cf. this vol., i, 402, 709, 710).—The swelling of cellulose acetate in mixtures of nitrobenzene and alcohol of various compositions has been investigated at 25°. It is shown that over the range of concentrations 12—60% nitrobenzene, this substance is taken up by the cellulose acetate in such an amount that there is a constant partition relationship between the amounts in the liquid and solid phases. The alcohol is combined in a constant amount with the cellulose acetate over a long range of the lower concentrations of nitrobenzene, but at higher concentrations, 60% and upwards, the solubility of the cellulose acetate in nitrobenzene exerts a disturbing influence on this relationship. J. F. S.

Polysaccharides. IX. Cellulose and Lignin. P. KARRER and F. WIDMER (*Helv. Chim. Acta*, 1921, **4**, 700—702).—Treatment of dry cellulose with acetyl bromide free from acetic acid yields a mixture of amorphous products containing bromine. Acetobromocellose and -glucose are only formed in presence of acetic acid, and in proportions which, although notable (20% of the former as a maximum by working at 40—50°), are far from quantitative, a point which differentiates cellulose from starch (cf. this vol., i, 768). The result permits of no decision as to whether cellulose is a polymeric anhydro-sugar or possesses a chain structure, since the conditions mentioned are too drastic, and at low temperatures very little

acetobromocellose is produced. Wood, straw, and similar materials are completely dissolved by acetyl bromide. The solutions, when decomposed by ice, furnish decomposition products of cellulose and of lignin, from which the former may be removed by solution in alcohol, leaving the latter as a powder which contains bromine and does not reduce Fehling's solution. The result supports the view that lignin and cellulose are not chemically combined in wood.

J. K.

Constitution of Lignin. S. V. HINTIKKA (*Cellulosechemie*, 1921, **2**, 63—64; from *Chem. Zentr.*, 1921, iii, 619).—The contention of Klason (A., 1920, i, 474 and 821) that an acraldehyde complex, R·CH:CH:CHO, occurs in lignin and that in the sulphite process a sulphonic acid, $CH_2R·CH(SO_2·OH)·CHO$, is first formed which gives a yellow cyclic salt with naphthylamine salts is regarded as untenable.

G. W. R.

Lignin from Straw prepared by Treatment with Alkali Carbonate. F. PASCHKE (*Zeitsch. angew. Chem.*, 1921, **34**, 465).—The lignin was prepared by treatment of the straw with an alkali carbonate, precipitation from the extract with acid, and purification by repeated solution in alkali and reprecipitation with acid. The equivalent weight, determined by solution of the purified lignin in excess of standard alkali hydroxide solution and titration with phenolphthalein and methyl-orange as indicators, with which lignin behaves similarly to carbonic acid, gave a value of 357, considerably lower therefore than the figure 462 found by Beckmann (this vol., i, 546) for lignin from winter rye straw. This high figure was partly due to colloidal lignin passing through the filter in the method he adopted. Elementary analyses of the straw lignin gave figures corresponding with either $C_{27}H_{31}O_9$ or $C_{40}H_{45}O_{13}$, from which it is apparent that this lignin differs from Beckmann's essentially in its oxygen content, the formula assigned for the latter being $C_{40}H_{46}O_{15}$ (*loc. cit.*). The $C_{40}H_{45}O_{13}$ formula demands an equivalent weight of 366, assuming 1Na for each 20 C atoms. This is in close agreement with the value actually found.

G. F. M.

Unsaturated Residues in Chemical and Pharmacological Relationship. III. JULIUS VON BRAUN and OTTO BRAUNSDORF (*Ber.*, 1921, **54**, [*B*], 2081—2088).—In previous communications (A., 1918, i, 162) it has been shown that the anæsthetising action of substances containing the tropan ring is greatly increased by the introduction of a double bond. The observations have now been extended to the novocaine group, in which it is found that a similar effect is produced by the replacement of the ethyl by the allyl or cinnamyl groups, but not by the furfuryl radicle.

Ethyl-β-hydroxyethylallylamine, $C_3H_5·NEt·CH_2·CH_2·OH$, a colourless liquid, b. p. 183—184°, is prepared in 40% yield by the action of molecular proportions of ethylene oxide and ethylallylamine in moist chloroform solution at 60°. It is converted by *p*-nitrobenzoyl chloride in warm benzene solution into β-p-*nitrobenzoyloxyethylethylallylamine*, $C_3H_5·NEt·CH_2·CH_2·O·CO·C_6H_4·NO_2$, a yellow liquid

which solidifies when strongly cooled (the oily *hydrochloride*, the *platinichloride*, orange-yellow needles, m. p. 155—156°, and *picrate*, yellow platelets, m. p. 107—108°, are described). The nitro-compound is reduced by stannous chloride and hydrochloric acid to β-p-*aminobenzoyloxyethylethylallylamine*, a viscous, yellow liquid [*platinichloride*, m. p. 205° (decomp.) after darkening at 195°; *picrate*, m. p. 137°; the *hydrochloride* is extremely hygroscopic].

Ethylamine reacts with cinnamyl bromide to give *dicinnamylethylamine*, m. p. 44—45°, b. p. 235—240°/9 mm. (the *picrate* has m. p. 125—126°, the *hydrochloride* is oily) and *cinnamylethylamine*, a colourless, mobile liquid, b. p. 129—131°/9 mm. (the *hydrochloride*, m. p. 163°, *platinichloride*, decomp. 206°, *picrolonate*, long prisms, m. p. 215—216°, and *picrate*, dark yellow leaflets, m. p. 120°, are described). The secondary base is transformed by ethylene oxide into *cinnamylethyl-β-hydroxyethylamine*, $CHPh{:}CH{\cdot}CH_2{\cdot}NEt{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, a colourless, moderately viscous liquid which is partly decomposed when distilled. The p-*nitrobenzoyl* compound of the latter is a viscous, yellow liquid which is best characterised by its *picrolonate*; it is reduced by stannous chloride and hydrochloric acid to *cinnamyl*-β-p-*aminobenzoyloxyethylethylamine*, a yellow liquid which does not give crystalline salts. The corresponding *acetyl* derivative and its *hydrochloride* and *picrate* are non-crystalline.

Furfurylethylamine, $C_4H_3O{\cdot}CH_2{\cdot}NHEt$, b. p. 168—170°, is converted by ethylene oxide into the corresponding β-*hydroxyethyl* derivative, a pale yellow liquid, b. p. 127°/12 mm. (the *picrate* and *picrolonate*, m. p. 159°, are described). The p-*nitrobenzoyl* compound of the latter is oily, but yields crystalline salts of which the *picrolonate*, m. p. 164°, and *picrate*, m. p. 119°, have been examined. β-p-*Aminobenzoyloxyethylfurfurylethylamine* is also a liquid; it yields an indistinctly crystalline *picrate*. H. W.

Behaviour of certain Acyl Derivatives of Allylamine towards Halogens. MAX BERGMANN, FERDINAND DREYER, and FRITZ RADT (*Ber.*, 1921, **54**, [*B*], 2139—2150).—The bromination of allylacetamide has been examined by Chiari (A., 1899, i, 325), who, in spite of the abnormal course of his experiments, considered the process to occur in the orthodox manner with the formation of the dibromo-derivative. This is now shown to be the case in part, but during the reaction a wandering of the acetyl group is also observed so that the change may be represented by the scheme:

$$NHAc{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br \xleftarrow{\text{addition}} NHAc{\cdot}CH_2{\cdot}CH{:}CH_2 \xrightarrow[+H_2O]{\text{transformation}}$$

$CH_2Br{\cdot}CH(OAc){\cdot}CH_2{\cdot}NH_2,HBr$. A similar transformation is observed with the corresponding benzoyl and, to a less extent, with the bromoacetyl derivative, but not with the urethane. It is a matter of indifference whether bromination is effected with dry or moist substances. The dibromides are converted into the hydrobromides when heated alone or in the presence of water, so that it appears that they themselves or their precursors play a decisive part in the formation of the hydrobromides during the bromination of acylallylamines. This view is maintained, although it is

shown that the pre-formed dibromides are perfectly stable under the experimental conditions of the bromination and is justified by a series of examples taken from the literature by which it is shown that the stability of a compound in a state of rest cannot be taken as a criterion of its stability when formed under certain conditions of reaction.

Benzoallylamide is converted by bromine in moist chloroform solution into a mixture of benzo-N-βγ-dibromo-*n*-propylamide, m. p. 135°, and *γ-bromo-α-amino*iso*propyl benzoate hydrobromide*, $CH_2Br\cdot CH(OBz)\cdot CH_2\cdot NH_2,HBr$, colourless, microscopic needles, m. p. 188—189° (decomp.) after previous softening when rapidly heated. If the salt is treated with sufficient alkali to neutralise the hydrobromic acid, the liberated base rapidly becomes isomerised to *benzo-γ-bromo-β-hydroxypropylamide*, thin, hexagonal plates, m. p. 115°, the p-*nitrobenzoate* of which forms microscopic needles, m. p. 146°. Similarly, the chlorination of benzoallylamide yields benzo-βγ-dichloropropylamide and relatively larger amounts of α-chloro-β-benzoxypropylamine hydrochloride which was analysed in the form of its *picrate*, m. p. 181°.

The bromination of acetoallylamide leads to the formation of aceto-βγ-dibromo-*n*-propylamide, m. p. 65° (indefinite), and *γ-bromo-β-acetoxypropylamine hydrobromide*, long needles, m. p. 159—161° (*picrate*, short, rhombic prisms, m. p. 124—126°); the latter substance is also formed by the transformation of the dibromide in the presence of water at 100°.

N-Allylurethane is transformed by bromine into N-*βγ-dibromo*-n-*propylurethane*, $CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO_2Et$, short needles, m. p. 44°.

Bromination of *bromoacetoallylamide*, b. p. 85°/0·3—0·4 mm., leads to the production of *bromoaceto-βγ-dibromo*-n-*propylamide*,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO\cdot CH_2Br,$$

needles or prisms, m. p. 77—79°, and *α-bromo-β-bromoacetoxypropylamine hydrobromide*, $CH_2Br\cdot CH(O\cdot CO\cdot CH_2Br)\cdot CH_2\cdot NH_2,HBr$, irregular quadratic plates, m. p. 150°; the latter substance is also obtained when the dibromide is boiled with water. The corresponding *picrate* crystallises in small, yellow prisms, m. p. 154—156°. The hydrobromide is transformed by the equivalent quantity of *N*-sodium hydroxide solution into *bromoaceto-γ-bromo-β-hydroxypropylamide*, $CH_2Br\cdot CH(OH)\cdot CH_2\cdot NH\cdot CO\cdot CH_2Br$, thin, rhombic plates, m. p. 86—87°. H. W.

Preparation of Additive Products of Hexamethylenetetramine. J. D. RIEDEL, AKT. GES. (D.R.-P. 338427; from *Chem. Zentr.*, 1921, iv, 588—589).—The additive products obtained from monohalogen acetic acids and hexamethylenetetramine (D.R.-P. 334709) are rather unstable in solution. Their metallic salts, which are more stable, are prepared by usual methods. G. W. R.

Preparation of Derivatives of Hexamethylenetetramine. J. D. RIEDEL AKT. GES., and FR. BOEDECKER (D.R.-P. 338428; from *Chem. Zentr.*, 1921, iv, 589; cf. preceding abstract). —Hexamethylenetetramine is allowed to react with metallic

salts of monohalogen acetic acids whereby quaternary salts are formed. G. W. R.

Synthesis of Formamide from Carbon Monoxide and Ammonia. KURT H. MEYER and LUDWIG ORTHNER (*Ber.*, 1921, **54**, [*B*], 1705—1709).—Formamide is obtained in small amount by heating carbon monoxide and ammonia in a steel tube in the presence of porous clay at 200° under a final pressure of 170 atmospheres. Ammonium carbonate, formate, and cyanide are produced simultaneously. Below 180°, the rate of reaction is too small, whilst above 200° the yields are too low; formamide is almost completely decomposed at 227°. H. W.

Bromural [α-Bromo*iso*valerylcarbamide]. E. YOSHITOMI and K. WATANABE (*J. Pharm. Soc. Japan*, 1921, No. **468**, 125—130).—In the preparation of α-bromo*iso*valerylcarbamide by way of *iso*amyl alcohol, *iso*valeric acid, and α-bromo*iso*valeryl bromide, condensation products of carbamide with α-methylbutyric acid and *iso*valeric acid are also formed. The commercial product has m. p. 145—156°, whereas the pure substance has m. p. 154°. It is shown, however, that m. p. determinations will not indicate the purity of bromural when *iso*valerylcarbamide is present as an impurity. CHEMICAL ABSTRACTS.

α-Bromohexoylcarbamide and Homologous Straight Chain Bromoacyl Derivatives of Carbamide. M. TIFFENEAU and ET. ARDELY (*Bull. Sci. Pharmacol.*, 1921, **28**, 155—160; from *Chem. Zentr.*, 1921, iii, 366).—In a study of the bromoacyl derivatives of carbamide the following compounds were prepared: *α-Bromohexoylcarbamide*, $CH_2Me\cdot[CH_2]_2\cdot CHBr\cdot CO\cdot NH\cdot CO\cdot NH_2$, prepared from bromohexoyl chloride and carbamide; it crystallises in fine needles, m. p. 134°; α-hydroxyhexoylcarbamide is formed on boiling with water. α-Bromoheptoylcarbamide has m. p. 136°. *α-Bromononoylcarbamide* crystallises in silky needles, m. p. 176°. *α-Bromolaurylcarbamide* forms fibrous masses, m. p. 186°. Straight-chain derivatives have a simple diuretic action without any hypnotic effect. The physiological effect of other derivatives is to be attributed to branched chains rather than to the presence of halogen. G. W. R.

Ethyl- and Allyl-selenocarbamides and their Alkyl Haloids. HANS SCHMIDT (*Ber.*, 1921, **54**, [*B*], 2067—2070).—*Ethylselenocarbamide*, $NHEt\cdot CSe\cdot NH_2$, colourless needles, m. p. 125°, is prepared by treating a solution of ethylcyanamide in anhydrous ether with hydrogen selenide at the atmospheric temperature in the absence of air and in subdued light. The substance rapidly becomes red owing to the separation of selenium when exposed to light, but can be preserved indefinitely in sealed vessels in the dark. The selenium atom is far more labile than is the sulphur atom in the corresponding thio-compound. The substance unites with allyl bromide in alcoholic solution at 60—70°, giving the additive *product*, $NHEt\cdot C(NH_2)\!:\!SeBr\cdot C_3H_5$, or $NHEt\cdot C(\!:\!NH)\cdot Se\cdot C_3H_5,HBr$, m. p. 115°. *Allylselenocarbamide* forms colourless crystals, m. p.

about 93°, and has an intensely irritant effect on the skin; with ethyl iodide, it yields a colourless, additive *compound*, $C_6H_{13}N_2ISe$, m. p. 100°. H. W.

The Constitution of Hydrocyanic Acid. KURT H. MEYER and HEINRICH HOPFF (*Ber.*, 1921, **54**, [*B*], 1709—1714).—Adopting a method similar to that used with ethyl acetoacetate (A., 1920, i, 717), the authors have endeavoured to separate anhydrous hydrocyanic acid into two different fractions, but without success, since the separate portions are found to have a constant refractive index ($n_D^{10\cdot0}$ 1·2715). Hydrocyanic acid cannot therefore be a mixture of two isomerides with a finite velocity of transformation and, since the molecular refraction of the liquid is identical with that of the gaseous acid, it is very improbable that it can be a mixture with high velocity of interconversion. The possibility of the presence of a small amount of the *iso*-form, as exhibited by ethyl malonate and methanetricarboxylate (A., 1912, i, 941), is not, however, excluded. Attempts to deduce the constitution of the acid from physical data are recorded; the substance has $d_4^{10\cdot0}$ 0·7018 ($\pm$0·0002), n_D 1·2675, n_α 1·2661, n_β 1·2713, n_γ 1·2752, $n_\gamma - n_\alpha$ 0·0091, and comparison of these values with those calculated for the nitrile and *iso*nitrile forms indicates that free hydrocyanic acid is identical with formonitrile. Considerations of thermochemical data (cf. Lemoult, A., 1907, ii, 10) indicate that, at the atmospheric temperature, hydrocyanic acid is formonitrile containing minute amounts of carbylamine and that the proportion of the latter increases somewhat with increasing temperature. H. W.

Oxalic Acid Derivatives of "Diacetonitrile." ERICH BENARY and MAX SCHMIDT (*Ber.*, 1921, **54**, [*B*], 2157—2168.)—Diacetonitrile is shown to behave towards ethoxalyl chloride and ethyl oxalate in the same manner as ethyl β-aminocrotonate (A., 1917, i, 252).

N-Ethoxalyldiacetonitrile (cf. Fleischhauer, A., 1893, i, 396), m. p. 93°, is proved definitely to be a N-derivative by its conversion into *diacetonitrile*-N-*oxalphenylhydrazide*,

NHPh·NH·CO·CO·NH·CMe:CH·CN,

yellow needles, m. p. 192° (decomp.), which is decomposed by boiling dilute sulphuric acid with formation of oxalamidephenylhydrazide, m. p. 235°. C-*Ethoxalyldiacetonitrile*,

NH_2·CMe:C(CN)·CO·CO_2Et,

long, colourless needles, m. p. 114—115°, is obtained by the interaction of diacetonitrile, pyridine, and ethoxalyl chloride in absolute ethereal solution; the corresponding *amide*, colourless, pointed needles which carbonise above 195°, and *anilide*, lustrous, yellow leaflets, decomp. 203—207°, are described. The ester is slowly transformed by concentrated hydrochloric acid at the atmospheric temperature into *diacetonitrile*-C-*oxaliminolactone*,

$$\begin{array}{l}\text{NH:CMe·CH·C(NH)}\\ \quad\quad\quad\;\;\; | \quad\quad\quad\quad\; \searrow \\ \quad\quad\quad\;\; \text{CO}\text{——}\text{CO}\!>\!\text{O},\end{array}$$

colourless, hexagonal pyramids, incipient decomp. 230°; the same substance is obtained when the ester is treated with the calculated

quantity of sodium hydroxide, barium hydroxide, or sodium carbonate solution, but a portion of it is also decomposed into oxalic acid and ammonia. It is converted by aniline in boiling dilute acetic acid solution into the corresponding *anilino*-derivative,

$$\begin{array}{l}\mathrm{NPh{:}CMe{\cdot}CH{\cdot}C(NH)} \\ \quad\quad\;\, \mathrm{CO\text{——}CO}\end{array}\!\!>\mathrm{O},$$

golden-yellow, lustrous leaflets, m. p. 236°. Diacetonitrile-C-oxamide is slowly transformed by boiling water into *ammonium diacetonitrile*-C-*oxalate*, colourless four-sided prisms ($+H_2O$), decomp. 180—220° (the corresponding *silver* and *copper* salts are described); *diacetonitrile*-C-*oxalic acid*, $NH{:}CMe{\cdot}CH(CN){\cdot}CO{\cdot}CO_2H$, is isolated from the copper salt in the form of small, yellow crystals which are too hygroscopic to permit analysis or determination of the melting point.

C-Ethoxalyldiacetonitrile and phenylhydrazine in 50% acetic acid solution give 4-*cyano*-1-*phenyl*-3-*methylpyrazole*-5-*carboxylophenylhydrazide*,

$$\begin{array}{l}\mathrm{CMe{\cdot}C(CN)} \\ \mathrm{N\text{——}NPh}\end{array}\!\!>\mathrm{C{\cdot}CO{\cdot}NH{\cdot}NHPh},$$

colourless, rectangular leaflets, m. p. 207°, which is hydrolysed by sodium hydroxide solution to 4-carboxy-1-phenyl-3-methylpyrazole-5-carboxyphenylhydrazide, pointed needles, m. p. 253°, which is identical with the acid prepared previously (*loc. cit.*) by hydrolysis of the compound formed from ethyl β-aminocrotonate and phenylhydrazine. The cyano-compound is oxidised by potassium permanganate in acetone solution to 4-*cyano*-1-*phenyl*-3-*methylpyrazole*-5-*carboxylic acid*, colourless, four-sided prisms, m. p. 211—212° (decomp.), which passes when heated into 4-*cyano*-1-*phenyl*-3-*methylpyrazole*, prisms, m. p. 93—94°. The cyanocarboxylic acid is converted by sodium hydroxide solution into the previously described 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid.

The *diphenylhydrazone* of β-*ketobutyronitrile*-α-*oxamide*,

$$NHPh{\cdot}N{:}CMe{\cdot}CH(CN){\cdot}C({:}N{\cdot}NHPh){\cdot}CO{\cdot}NH_2,$$

prepared from C-ethoxalyldiacetonitrile and phenylhydrazine in boiling alcoholic solution, forms long, pointed needles, m. p. 232°. 4-*Cyano*-1-*phenyl*-3-*methylpyrazole*-5-*carboxyanilide*, from *diacetonitrile*-O-*oxanilide* and phenylhydrazine in boiling alcoholic solution, crystallises in colourless needles, m. p. 167—168°. H. W.

The Reducing Action of the Grignard Reagent and the Existence of Magnesium Hydrogen Haloid. KURT HESS and HEINRICH RHEINBOLDT (*Ber.*, 1921, **54**, [*B*], 2043—2055).—A series of experiments is described which has for its object the preparation of magnesium hydrogen haloids, H·Mg·Hal. It is found that, under the conditions customary in the preparation of Grignard's reagents, magnesium does not react with gaseous hydrogen chloride in the presence of ether or benzene. Liquid hydriodic acid does not attack magnesium whereas in the presence of dry ether a reaction occurs readily which, however, is due to the ready conversion of ether into ethyl iodide by hydrogen iodide. To avoid complications of this type, the "individual" Grignard compounds were used, when it was found that magnesium ethyl iodide does not react with gaseous or liquid hydrogen iodide, alone

or in the presence of benzene, whereas it is decomposed completely by hydrogen chloride with the liberation of ethane. Attempts to demonstrate the unaltered nature of the magnesium ethyl iodide after treatment with hydrogen iodide by bringing it into reaction with benzaldehyde led to the rather surprising isolation of benzyl alcohol instead of the expected phenylethylcarbinol. A similar result was observed with untreated magnesium ethyl iodide in warm benzene and, but to a less extent, in warm ether, whereas phenylethylcarbinol was exclusively obtained in ethereal solution at the atmospheric temperature.

Individual cases of reduction by Grignard's reagent have been recorded previously, but have not received any general explanation. According to the authors, they can be represented most accurately by the co-ordination formulæ, $RR'C\colon O\cdots Mg{<}^{Br}_{CH_2\cdot CH_3}$, and the reactions then occur in accordance with the scheme:

$$Mg{<}^{X}_{OH} + {}^{R}_{R'}{>}C{<}^{OH}_{CH_2\cdot CH_3} \xleftarrow[+H_2O]{\text{in the cold}} {}^{R}_{R'}{>}C\colon O\cdots Mg{<}^{X}_{CH_2\cdot CH_3}$$

$$\xrightarrow{\text{warmed}} {}^{R}_{R'}{>}C\colon O\cdots Mg{<}^{X}_{H} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow{+H_2O} {}^{R}_{R'}{>}C{<}^{OH}_{H} + Mg{<}^{X}_{OH}.$$

Since it is shown that the subsidiary reaction may be made into the main change by increasing the temperature, it is possible that a method is opened out for the reduction of substances containing the ketonic group and other reducible groups (for example, ethylenic linkings) which are not changed by reduction of the ketonic group. In any case, it is demonstrated that the avoidance of subsidiary reactions in the case of the aliphatic alkyl haloids (except the methyl compounds) can only be secured by the avoidance of elevated temperature, except under perfectly definite conditions. H. W.

The Benzene [Formula] Problem. V. The Benzene Ring in Substitution Products. A. VON WEINBERG (*Ber.*, 1921, **54**, [*B*], 2171—2175).—The introduction of a substituent into the benzene ring causes an alteration in the aromatic character the extent of which depends on the nature, number, and position of the substituents. It is shown by a series of examples that the abnormal deviations can be considered mathematically in the cases of the molecular refraction, absorption spectra, and energy content. Increase in volume (as indicated by molecular refraction) is accompanied by increase in the wave-length of the absorption band of maximal intensity and by a parallel decrease of the energy content. H. W.

Nitrogen Dioxide. I. Nitration with Nitrogen Dioxide. HEINRICH WIELAND [with C. REISENEGGER] (*Ber.*, 1921, **54**, [*B*], 1776—1784; cf. Wieland and Blümich, this vol., i, 552).—The behaviour of nitrogen dioxide towards aromatic compounds has been investigated.

Pure nitrogen dioxide does not react with cold aromatic hydrocarbons; with benzene at 80°, the main products are 1 : 3 : 5-trinitrobenzene and picric acid, together with smaller amounts of unchanged benzene, nitrobenzene, carbon dioxide, oxalic acid, and nitrogenous substances which are soluble in water and belong to the fatty series. The production of the trinitro-derivatives in the presence of unchanged benzene indicates that the process is one of primary addition to a hexanitro-derivative followed by elimination of nitrous acid and not of step-wise nitration; this is confirmed further by the observation that nitrobenzene is indifferent towards nitrogen dioxide at 80°.

[With A. BERNHEIM and P. BÖHM.]—Phenol is readily nitrated when dissolved in a cold mixture of benzene and light petroleum and treated with a solution of nitrogen dioxide in the same solvents; a mixture of *o*- and *p*-nitrophenols is obtained, the total weight of which is 125% of that of the phenol used. Tarry by-products are not observed. *o*-Cresol yields *o*- and *p*-nitro-*o*-cresol, *m*-cresol gives *o*- and *p*-nitro-*m*-cresol, whilst the *p*-compound yields *o*-nitro-*p*-cresol and *o*-dinitro-*p*-cresol. *m*-4-Xylenol is converted into the corresponding 5-nitro-compound. α-Naphthol gives a mixture of 2-nitro-α-naphthol and 2 : 4-dinitro-α-naphthol. Reaction does not occur with anisole.

Acetanilide does not suffer nitration in the nucleus; the acetyl group is removed and benzenediazonium nitrate results.

The action of nitrogen dioxide on diphenylamine depends greatly on the solvent used; with ether, it is converted into diphenylnitrosoamine, whereas in the presence of benzene it gives *p*-nitrodiphenylnitrosoamine. In the former case the reaction is explained by the observation that absolute ether reacts readily with nitrogen dioxide with the formation of ethyl nitrite, $Et_2O + N_2O_4 \longrightarrow EtO{\cdot}NO + EtO{\cdot}NO_2$; in the latter instance, the primary action doubtless consists of nitration in the nucleus, the nitroso-group being introduced subsequently by the liberated nitrous acid.

The constitution of nitrogen trioxide and peroxide is discussed; the conception of the latter as a mixed anhydride of nitrous and nitric acids, $O{:}N{\cdot}O{\cdot}NO_2$, is in harmony with its action towards alkali, but the similar conception of nitrogen trioxide as $O{:}N{\cdot}O{\cdot}N{:}O$ is not in keeping with its intense blue colour in accordance with which it must be regarded as a nitroso-derivative, $O{:}N{\cdot}NO_2$. The corresponding formula, $O_2N{\cdot}NO_2$, is also very probable for the peroxide by reason of its reactions and dissociability; its decomposition by alkali is then analogous to that of other symmetrically-paired atoms or radicles, for example, cyanogen to cyanide and cyanate, chlorine to chloride and hypochlorite. H. W.

Transformation or (and) Hydrolysis of the Toluene-*p*-sulphonyl Compounds of certain *para*-Substituted Anilines and their N-Alkyl Derivatives. J. HALBERKANN (*Ber.*, 1921, **54**, [*B*], 1833—1849).—In a previous communication (this vol., i, 661) it has been shown that *p*-toluenesulphonyl-*p*-anisidide is convertible by sulphuric acid into 2-amino-5-methoxyphenyl-*p*-

tolylsulphone and thus forms an exception to Witt's rule (A., 1913, i, 360; 1914, i, 228), according to which the sulphonamides of primary bases only suffer hydrolysis, whilst those of secondary bases suffer transformation. A more extended study has confirmed the general validity of the rule in so far as the primary bases are concerned, and has shown that the behaviour of the *p*-anisidide is exceptional. In its present form, however, the statement of the rule is too general in the case of the sulphonamides of secondary bases; many of these readily undergo hydrolysis with the production of pure secondary bases and all of them can be caused to do so by the use of suitably dilute sulphuric acid, thus giving the simplest method available at present for the preparation of pure secondary amines.

Toluene-*p*-sulphonyl-*p*-toluidide is converted by sulphuric acid (*d* 1·84) at 130° into *p*-toluidine-*o*-sulphonic acid and by rapid treatment at 55° into small amounts of *o*-aminodi-*pp'*-tolylsulphone, m. p. 166°; with the acid (*d* 1·74) at 130°, *p*-toluidine (88%), together with traces of the sulphone and toluidinesulphonic acid, is produced, whilst the 70% acid causes quantitative hydrolysis to *p*-toluidine. N-p-*Toluenesulphonylmethyl*-p-*toluidide*, $C_6H_4Me{\cdot}NMe{\cdot}SO_2{\cdot}C_6H_4Me$, large, colourless rods, m. p. 60° (from the preceding compound and methyl sulphate in alkaline solution), is almost quantitatively converted by the action of sulphuric acid (*d* 1·84) at 100° into 6-*methylamino*-m-*tolyl*-p-*tolylsulphone*, $C_6H_4Me{\cdot}SO_2{\cdot}C_6H_3Me{\cdot}NHMe$, colourless, fluorescent, prismatic plates, m. p. 138° (corresponding *acetyl* derivative, colourless, prismatic needles, m. p. 149—150°); with sulphuric acid (*d* 1·74) at 120°, N-methyl-*p*-toluidine is mainly produced together with small amounts of the sulphone, whilst the acid (*d* 1·67) causes quantitative hydrolysis. N-*p*-Toluenesulphonylethyl-*p*-toluidide, coarse, colourless prisms, m. p. 51—52° (Witt, *loc. cit.*, gives m. p. 71—72°), behaves similarly to the methyl compound. *Toluene*-p-*sulphonyl*-p-*nitroanilide*, yellow prisms, m. p. 191° (from the components in the presence of pyridine), is hydrolysed by sulphuric acid (*d* 1·84, 1·74, or 1·6). N-*p*-Toluenesulphonylmethyl-*p*-nitroanilide, yellow prisms, m. p. 176° (Morgan and Micklethwait, T., 1912, **101**, 146, give m. p. 182°), could not be isomerised to the sulphone, but is smoothly converted into N-methyl-*p*-nitroaniline. Similarly, isomerisation could not be induced in the cases of toluene-*p*-sulphonyl-*p*-aminoanilide or N-*p*-toluenesulphonylmethyl-*p*-aminoanilide, from which the corresponding bases are produced quantitatively. Toluene-*p*-sulphonyl-*p*-sulphonanilide,

$$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H,$$

is obtained in the form of its *pyridine* salt, long, colourless, prismatic needles ($+1H_2O$), m. p. 177°; it is quantitatively hydrolysed to sulphanilic acid by sulphuric acid (*d* 1·84) at 95° or (*d* 1·74) at 110°. *Sodium* p-*toluenesulphonylmethylsulphanilate*, $C_6H_4Me{\cdot}SO_2{\cdot}NMe{\cdot}C_6H_4{\cdot}SO_3Na$, colourless, slender needles ($+2H_2O$), decomp. about 295°, is hydrolysed by sulphuric acid (*d* 1·84 or 1·74) to N-*methyl*-p-*sulphanilic acid*, colourless, lustrous plates, m. p.

244—245° (decomp.). Toluene-*p*-sulphonyl-*p*-chloroanilide, m. p. 95—96° (*acetyl* compound, long, prismatic needles, m. p. 154°), could not be isomerised. p-*Toluenesulphonylmethyl*-p-*chloroanilide*, colourless crystals, m. p. 96—97°, is almost quantitatively hydrolysed by sulphuric acid to N-methyl-*p*-chloroaniline, b. p. 242°/768 mm.; small amounts (6%) of 5-*chloro*-2-*methylaminophenyl*-p-*tolylsulphone*, $C_6H_4Me{\cdot}SO_2{\cdot}C_6H_3Cl{\cdot}NHMe$, colourless prisms, m. p. 156° (*acetyl* derivative, m. p. 157—158°), are produced simultaneously. H. W.

The Benzene [Formula] Problem. IV. The Naphthalene Formula. A. VON WEINBERG (*Ber.*, 1921, **54**, [*B*], 2168—2171).—The theory of intramolecular vibration has led the author previously (A., 1919, i, 314) to assign a symmetrical formula to naphthalene. The unsymmetrical formulæ of von Auwers and Frühling (this vol., ii, 230) and of Mayer and Bansa (this vol., i, 175) are criticised. The following is propounded as a safe empirical rule for the recognition of aromatic nuclei: " Only aromatic amino-derivatives yield diazo-compounds which can be coupled to azo-dyes and only in the case of aromatic substances is it possible to introduce a hydroxyl group by sulphonation and subsequent fusion with alkali." From both points of view, the symmetrical, purely aromatic structure of benzene appears to be one of the most firmly established facts of organic chemistry.

The author's formula for naphthalene involves the assumption that the β-carbon atoms are in more intense vibration than the α-carbon atoms; evidence in favour of this view is found in von Auwers and Frühling's measurements of a number of α- and β-derivatives of naphthalene. H. W.

The Fluorene Series. V. 2 : 7-Dichlorofluorene. A. SIEGLITZ and J. SCHATZKES (*Ber.*, 1921, **54**, [*B*], 2072—2078).—It has been shown previously (A., 1920, i, 605) that the methylene group of 2 : 7-dibromofluorene is considerably more reactive than that of the parent hydrocarbon; this is now shown to be also true of 2 : 7-dichlorofluorene.

2 : 7-Dichlorofluorene, flat plates or needles, m. p. 128°, is prepared according to the directions of Hodgkinson and Matthews (T., 1883, **43**, 170) and the position of the halogen atoms is proved definitely by conversion of the substance into 2 : 7-dichlorofluorenone. It condenses with the requisite aldehyde in boiling alcoholic solution in the presence of sodium ethoxide to yield the following derivatives (2 : 2′ : 7 : 7′-*tetrachloro*-αδ-*dibiphenylene*-$\Delta^{\alpha\gamma}$-*butadiene*, small, cinnabar-red needles which do not melt below 300°, is invariably formed as by-product) : 2 : 7-*dichloro*-9-*benzylidenefluorene*, pale yellow rods, m. p. 94°; 2 : 7-*dichloro*-9-o-*methylbenzylidenefluorene*, yellow rods, m. p. 142—143°; 2 : 7-*dichloro*-9-m-*methylbenzylidenefluorene*, pale yellow crystals, m. p. 96—97°; 2 : 7-*dichloro*-9-p-*methylbenzylidenefluorene*, long, lemon-yellow needles, m. p. 148°; 2 : 7-*dichloro*-9-p-iso*propylbenzylidenefluorene*,

pale yellow rods, m. p. 94—95°; 2 : 2′ : 7 : 7′-*tetrachloro*iso*phthalylidenedi*-9 : 9′-*fluorene*, bright yellow needles, m. p. 253—254°; 2 : 7-*dichloro*-9-p-*aldehydobenzylidenefluorene*, deep yellow needles, m. p. 204—205°; 2 : 2′ : 7 : 7′-*tetrachloro*-9 : 9′-*diterephthalylidenedifluorene*, egg-yellow needles which do not melt below 285°; 2 : 7-*dichloro*-9-o-*chlorobenzylidenefluorene*, slender, pale orange-yellow needles, m. p. 159—160°; 2 : 7-*dichloro*-9-m-*chlorobenzylidenefluorene*, yellow needles, m. p. 134—135°; 2 : 7-*dichloro*-9-p-*chlorobenzylidenefluorene*, matted, lemon-yellow needles, m. p. 204—205°; 2 : 7-*dichloro*-9-2′ : 6′-*dichlorobenzylidenefluorene*, canary yellow leaflets, m. p. 212—213°; 2 : 7-*dichloro*-9-m-*bromobenzylidenefluorene*, microscopic, yellow needles, m. p. 146—147°; 2 : 7-*dichloro*-9-p-*anisylidenefluorene*, long, dark yellow needles, m. p. 126—127°; 2 : 7-*dichloro*-9-*piperonylidenefluorene*, orange-yellow needles, m. p. 165°; 2 : 7-*dichloro*-9-o-*nitrobenzylidenefluorene*, microscopic, yellow needles, m. p. 173—174°; 2 : 7-*dichloro*-9-m-*nitrobenzylidenefluorene*, lemon-yellow needles, m. p. 180—181°; 2 : 7-*dichloro*-9-p-*nitrobenzylidenefluorene*, yellow needles, m. p. 196—197°; 2 : 7-*dichloro*-9-*cinnamylidenefluorene*, dark orange needles, m. p. 191°; 2 : 7-*dichloro*-9-*furfurylidenefluorene*, greenish-yellow needles, m. p. 190—191°; *ethyl* 2 :7-*dichloro*-9-*fluoreneglyoxylate*, lustrous, yellow needles, m. p. 155—156° (*benzoyl* derivative, m. p. 156—157°).

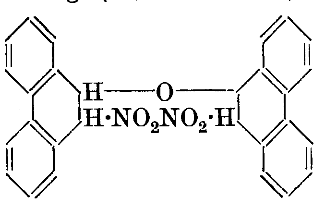
The following fulvanes of 2 : 7-dichlorofluorene are prepared by reduction of the corresponding fulvene with aluminium amalgam in moist ethereal solution: 2 : 7-*dichloro*-9-*benzylfluorene*, colourless leaflets, m. p. 110—111°; 2 : 7-*dichloro*-9-*methylbenzylfluorene*, colourless leaflets, m. p. 136—137°; 2 : 7-*dichloro*-9-p-iso*propylbenzylfluorene*, colourless needles, m. p. 115°; 2 : 7-*dichloro*-9-o-*chlorobenzylfluorene*, colourless leaflets, m. p. 116—117°; 2 : 7-*dichloro*-9-2′ : 6′-*dichlorobenzylfluorene*, long, colourless needles, m. p. 129—130°; 2 : 7-*dichloro*-9-p-*anisylfluorene*, colourless leaflets, m. p. 137—138°.

2-*Nitro*-9-p-*chlorobenzylidenefluorene* crystallises in dull yellow, microscopic needles, m. p. 246°. H. W.

Nitration. HEINRICH WIELAND and FRANZ RAHN (*Ber.*, 1921, **54**, [*B*], 1770—1775).—It has been shown previously (Wieland and Sakellarios, A., 1920, i, 280) that ethylene is converted by nitrating acid into a mixture of ethylene dinitrate and β-nitroethyl nitrate, and hence that the primary process of nitration is the same in the aliphatic as in the aromatic series. In this instance, however, simultaneous esterification which is guaranteed by the presence of sulphuric acid is necessary for the protection of the product against further oxidation. In the present communication, a number of instances is recorded in which nitric acid is added directly at an aliphatic double bond; the most remarkable feature is the striking readiness with which such addition occurs.

αα-Diphenylethylene is converted by absolute nitric acid in carbon tetrachloride solution at −10° into β-nitro-αα-diphenylethyl alcohol, $OH\cdot CPh_2\cdot CH_2\cdot NO_2$, colourless crystals, m. p. 106°, which is identical with the substance described by Anschütz and

Romig (A., 1886, 1033) as "diphenylglycol mononitrite" (cf. also Anschütz and Hilbert, following abstract). In a similar manner, phenanthrene gives the ether (annexed formula), colourless, slender needles, m. p. 167° (cf. Schmidt, A., 1901, i, 76). The primary product of the action of nitric acid on β-methyl-Δ^{β}-butylene could not be isolated, the reaction leading to the production of γ-nitro-β-methyl-Δ^{β}-butylene, $CMe_2{:}CMe{\cdot}NO_2$, an almost colourless liquid, b. p. 79—80°/17 mm., and *nitro*iso*amyl nitrate*, b. p. 135°/17 mm.



[With F. Reindel.]—A solution of αα-diphenylethylene in light petroleum is transformed by nitrogen peroxide into *αβ-dinitro-αα-diphenylethane*, colourless needles, m. p. 68°, which is converted by sodium hydroxide solution into β-nitro-αα-diphenylethylene, m. p. 87° (cf. Anschütz and Romig, *loc. cit.*). The remarkable rapidity with which nitric acid is added at the double bond is illustrated by the observation that β-nitro-αα-diphenylethyl alcohol is the sole product of the action of nitrogen peroxide on αα-diphenylethylene if extreme care in excluding the presence of every trace of moisture is not taken. H. W.

Action of Nitric Acid on αα-Diphenylethane and αα-Diphenylethylene. Richard Anschütz and Alfred Hilbert (*Ber.*, 1921, **54**, [*B*], 1854—1859).—In connexion with the recent publication of Wieland and Sakellarios (A., 1920, i, 280; cf. Wieland and Rahn, preceding abstract), the authors have repeated the work of Anschütz and Romig (A., 1886, 1033) on the nitration of αα-diphenylethane and αα-diphenylethylene in glacial acetic acid solution. The products described previously as diphenylethylene glycol mononitrite, diphenylvinyl nitrite, and "dinitrite" are shown to be β-nitro-αα-diphenylethyl alcohol, β-nitro-αα-diphenylethylene, and ββ-dinitro-αα-diphenylethylene respectively, the course of the change being indicated by the scheme: $CPh_2{:}CH_2 \xrightarrow{+HNO_3} OH{\cdot}CPh_2{\cdot}CH_2{\cdot}NO_2 \xrightarrow{-H_2O} CPh_2{:}CH{\cdot}NO_2 \xrightarrow{+HNO_3} OH{\cdot}CPh_2{\cdot}CH(NO_2)_2 \xrightarrow{-H_2O} CPh_2{:}C(NO_2)_2$. The reduction of the latter to diphenylacetonitrile occurs in the following manner: $CPh_2{:}C(NO_2)_2 \xrightarrow{12H} CPh_2{:}C(NH_2)_2 \xrightarrow{-NH_3} CPh_2{:}C{:}NH \longrightarrow CHPh_2{\cdot}CN$. The same substances are also produced from diphenylethane; this is due to oxidation of the latter to diphenylmethylcarbinol, which is converted with loss of water into diphenylethylene.

The authors give a facsimile of a private communication of Kekulé which shows that the latter, in 1877, considered the product of the action of nitric acid on ethylene to be nitroethyl nitrate. H. W.

Reduction of Organic Halogen Compounds. IV. The Tetra-arylbutane Series and ααδδ-Tetraphenylbutatriene. K. Brand (*Ber.*, 1921, **54**, [*B*], 1987—2006; cf. A., 1913, i, 1169, 1170).—Temporary inability to obtain the requisite supply of

electricity has led the author to continue his experiments with chemical reducing agents.

βββ-Trichloro-αα-diphenylethane is reduced by Devarda's or Arndt's alloy in boiling alcoholic (95%) solution to *ββγγ-tetrachloro-ααδδ-tetraphenylbutane*, $CHPh_2 \cdot CCl_2 \cdot CCl_2 \cdot CHPh_2$, colourless needles, m. p. 188—190°; acetaldehyde and tetraphenyldichlorobutene are also produced, whilst much βββ-trichloro-αα-diphenylethane remains unattacked. In general, the yields are not particularly good, and the method is less suitable than the electrochemical process. When treated similarly, βββ-tribromo-αα-diphenylethane gives a mixture of *ββγγ-tetrabromo-ααδδ-tetraphenylbutane*, colourless crystals, m. p. 196—197°, and probably of the stereoisomeric *βγ-dibromo-ααδδ-tetraphenyl-Δ^{β}-butenes*, colourless needles, m. p. about 130—131°. ββγγ-Tetrachloro-ααδδ-tetraphenylbutane is reduced by zinc dust in boiling glacial acetic acid solution to βγ-dichloro-ααδδ-tetraphenyl-Δ^{β}-butene, which is separable by fractional crystallisation from light petroleum and alcohol into the stereoisomeric *forms*, m. p. 106—108° and 137—138°, respectively; the fractions appear to be uniform under the microscope, but the melting points are not very definite. A similar elimination of two atoms of halogen occurs when the tetrachloro-compound is treated with zinc dust and alcohol or with hydrogen in the presence of palladianised calcium carbonate, or is reduced electrochemically at a lead cathode; in no case is the halogen replaced by hydrogen. ββγγ-Tetrabromo-ααδδ-tetraphenylbutane, on the other hand, loses the whole of its bromine when subjected to reduction, and is converted, for example, by zinc dust in boiling glacial acetic acid solution, into ααδδ-tetraphenyl-Δ^{β}-butinene, $CHPh_2 \cdot C \vdots C \cdot CHPh_2$, colourless needles, m. p. 116°. βγ-Dichloro-ααδδ-tetraphenyl-Δ^{β}-butene is remarkably stable towards bromine, chlorine, potassium permanganate, and chromic acid in glacial acetic acid solution, with the latter of which it yields benzophenone in very small amount. It is transformed by boiling alcoholic potassium hydroxide solution into *ααδδ-tetraphenyl-$\Delta^{\alpha\beta\gamma}$-butatriene*, $CPh_2{:}C{:}C{:}CPh_2$, long, yellow needles, m. p. 240°; the latter is oxidised quantitatively by chromic acid in glacial acetic acid solution to carbon dioxide and benzophenone, and is reduced by sodium and amyl alcohol to ααδδ-tetraphenylbutane, m. p. 121° (cf. Valeur, A., 1903, i, 416), and by amyl alcohol and amalgamated zinc wool to ααδδ-tetraphenyl-$\Delta^{\alpha\gamma}$-butadiene, long, colourless needles, m. p. 202° (cf. Valeur, *loc. cit.*). It is converted by exposure to strong sunlight into the *hydrocarbon*, $(C_{28}H_{20})_2$, yellow crystals with green fluorescence, m. p. 280°, the investigation of which is not yet complete. Purdie and Arup (T., 1910, **97**, 1538) have described a substance, colourless crystals, m. p. 157—158°, which they obtained by the distillation of 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydrofuran with zinc dust and considered to be ααδδ-tetraphenyl-$\Delta^{\alpha\beta\gamma}$-butatriene; this is not identical with the author's substance, and the reason for the difference has not been elucidated. A second *hydrocarbon*, orange-coloured platelets, m. p. 207—208°, to which the formula $C_6H_4{<}{\begin{smallmatrix}CPh{=}{=}\\C({:}CPh_2)\end{smallmatrix}}{>}CH$ is ascribed provisionally,

is isolated from the mother-liquors obtained in the preparation of tetraphenylbutatriene; it is oxidised by chromic acid in boiling glacial acetic acid solution to carbon dioxide, benzophenone, and *o*-benzoylbenzoic acid. H. W.

Reduction of Organic Halogen Compounds. VI. ααδδ-Tetra-aryl-Δ^{β}-butinene. K. BRAND (*Ber.*, 1921, **54**, [*B*], 2017—2021).—It has been shown previously (Brand, *Zeitsch. Elektrochem.*, 1910, **16**, 669) that βββ-trichloro-αα-diphenylethane is reduced in boiling alcoholic solution at a lead cathode to a compound, $C_4H_2Ph_4$, and later (Brand and Matsui, A., 1913, i, 1170), the similar *p*-tolyl and *p*-anisyl compounds have been prepared. At that time it was impossible to decide between the alternative formulæ, $CHPh_2·C⋮C·CHPh_2$ and $CHPh_2·CH⁚C⁚CPh_2$, for the parent substance, since it is indifferent towards bromine and, on oxidation, gives relatively greatly varying amounts of benzophenone and diphenylacetic acid. The preparation of these compounds by the reduction of ββγγ-tetrabromo-ααδδ-tetraphenylbutane and ββγγ-tetrabromo-ααδδ-tetra-*p*-anisylbutane (preceding abstract and this vol., i, 787) leaves no doubt that they have the structure

$$CHAr_2·C⋮C·CHAr_2.$$

The unusual course of the oxidation of the phenyl derivative is explained by the observation that it yields ααδδ-tetraphenyl-$\Delta^{\alpha\beta\gamma}$-butatriene when treated with calcium permanganate in well-cooled, aqueous pyridine solution: $CHPh_2·C⋮C·CHPh_2 + O + H_2O \longrightarrow CHPh_2·C(OH)⁚C(OH)·CHPh_2 \longrightarrow CPh_2⁚C⁚C⁚CPh_2$.

The author's previous assumption that the reduction of trichlorodiphenylethane to the butinene hydrocarbon occurs through the successive stages, ββγγ-tetrachloro-ααδδ-tetraphenylbutane, and βγ-dichloro-ααδδ-tetraphenyl-Δ^{β}-butene, is rendered untenable by the observation that the latter substance is highly resistant to electrolytic reduction at a lead cathode. It now appears more probable that the primary action consists in the complete removal of chlorine from the ethane derivative, with formation of the radicles, $CHPh_2·C⋮$, which then unite in pairs with production of the butinene compound. H. W.

Keto-anils. I. Preparation of Aliphatic Keto-anils and Fission of Keto-anil Alkyliodides by Alkali. E. KNOEVENAGEL [with OTTO JÄGER] (*Ber.*, 1921, **54**, [*B*], 1722—1730).—A number of keto-anils have been prepared by the action of aromatic amines on aliphatic ketones in the presence of iodine. They are hydrolysed by acid with greater or less readiness, but are extremely stable towards alkali hydroxides. They combine readily with alkyl iodides, but the products formed are not the normal salts of quaternary ammonium bases, since, although they are stable towards hot acids, they are attacked readily by cold dilute alkalis, with the formation of substances which, according to analysis, are keto-anils into which the alkyl group has been introduced; pending the full elucidation of their constitution, it is proposed to term them "alkylketo-anils." Certain of the primary products of the action of alkyl iodides on keto-anils exhibit a gradual change in melting

point when preserved; this is explained by the hypothesis of isomerisation according to the scheme: $CMe_2{:}NMeI{\cdot}C_6H_4Me \longrightarrow$

$$CH_2{:}CMe{-}\overset{H\diagdown\diagup I}{N}Me{\cdot}C_6H_4Me \text{ or } Me_2C{-}\overset{H\diagdown\diagup I}{N}{\cdot}C_6H_4Me \text{ (with } CH_2 \text{ bridging C and N)}.$$

The same compound is obtained from either isomeride by the action of cold dilute alkali. The alkylketo-anils can also combine with alkyl iodide, giving normal quaternary ammonium iodides which are stable towards alkali and are transformed by silver oxide into the corresponding hydroxides; the latter lose alcohol when distilled and regenerate the alkylketo-anil.

The following individual substances are described: *Acetoneanil* (from the components and iodine under pressure at 180° or by protracted heating under a reflux condenser), a pale yellow liquid, b. p. 132°/13 mm., m. p. 23·5° [*hydrochloride*, m. p. 182—184°; *methiodide*, colourless crystals, m. p. 148°. *Methylacetoneanil*, a pale yellow liquid, b. p. 142°/13 mm., which yields a *hydrochloride*, m. p. 166—167°; a *hydriodide*, m. p. 139—141° and a *methiodide*, colourless crystals, m. p. 158° (decomp.)]. *Acetone*-p-*tolil*, a pale yellow liquid, b. p. 140°/11 mm., m. p. 36° [*methiodide*, m. p. 148° (decomp.), which rises when the substance is preserved during four weeks to 158°]. *Methylacetone*-p-*tolil*, a pale yellow liquid, b. p. 155°/14 mm. (*hydrochloride*, m. p. 164—165°; *hydriodide*, m. p. 80—82°; *methiodide*, colourless needles, m. p. 157·5—158·5°; *benzyliodide*, m. p. 198°). Acetone-*p*-tolil reacts with alkyl haloids with greatly varying velocity, yielding thus the *ethiodide*, colourless needles, m. p. 100—105°, n-*propiodide*, m. p. 116°, *benzylchloride*, m. p. 211—212°, and *benzyliodide*, m. p. 140—142°. *Benzylacetone*-p-*tolil* has m. p. 104—105°. *Acetone*-o-*tolil*, b. p. 138·5—139·5°/14 mm. (*hydrochloride*, m. p. 200—205°; *methiodide*, colourless crystals, m. p. 151°). *Acetone*-m-*tolil*, b. p. 143·5—144·5°/12 mm., m. p. 25°, (*hydrochloride*, m. p. 226—228°; methiodide, m. p. 159°). *Acetone*-o-*anisidil*, a glassy solid, b. p. 150—152°/13 mm. [*methiodide* (crude), m. p. 105—115°]. *Acetone*-o-*phenetidil*, m. p. 63° [methiodide (crude), m. p. 120—130°]. *Acetone*-p-*phenetidil*, a pale yellow liquid which solidifies to a vitreous mass, b. p. 169°/13 mm. (*methiodide*, m. p. 179°). *Methyl ethyl ketoanil*, b. p. 152—153°/14 mm. (*methiodide*, m. p. 208—211°, which when treated with dilute alkali gives a *liquid*, b. p. 157—164°/14 mm.). H. W.

Manufacture of Alkylamides of Aromatic Sulphonic Acids. British Cellulose and Chemical Mfg. Co., Ltd., Walter Bader, and Donald Archer Nightingale (Brit. Pat. 167941).—Aromatic sulphonalkylamides are obtained by the action of aromatic sulphonyl chlorides on alkylamine salts in presence of an alkali carbonate or other suitable acid neutralising agent, and a small quantity of water, preferably not exceeding 5% of the reaction mixture. For example, xylenesulphonmethylamide is obtained in almost theoretical yield by mixing together at 80—100° 1400 parts of xylenesulphonyl chloride, 470 parts of methylamine

hydrochloride, and 900 parts of sodium carbonate, the total moisture content not exceeding 5%. The product may conveniently be isolated by extraction with benzene followed by distillation in a vacuum. G. F. M.

Reduction of Organic Halogen Compounds. V. Phenol Ethers of the Tetraphenylbutane Series. K. BRAND and FRANZ KERCHER (*Ber.*, 1921, **54**, [*B*], 2007—2017).—The observations recorded in the preceding paper (this vol. i, 783) have been extended to the corresponding *pp'*-dimethoxy- and *pp'*-diethoxy-derivatives. The behaviour of the former is exactly similar to that of the parent substances, whereas the latter pass mainly into *pp'*-diethoxystilbene.

βββ-Trichloro-αα-di-*p*-anisylethane is converted by Devarda's or Arndt's alloy in boiling alcoholic solution (the success of the method depends considerably on the water content of the alcohol) into ββγγ-*tetrachloro*-αα$\delta\delta$-*tetra*-p-*anisylbutane*,

$$CH(C_6H_4{\cdot}OMe)_2{\cdot}CCl_2{\cdot}CCl_2{\cdot}CH(C_6H_4{\cdot}OMe)_2,$$

m. p. 204°, and dichlorotetra-anisylbutene. Under similar conditions, βββ-*tribromo*-αα-*di*-p-*anisylethane*, colourless needles, m. p. 113° (from bromal hydrate, anisole, and concentrated sulphuric acid in the presence of glacial acetic acid), yields ββγγ-*tetrabromo*-ααδδ-*tetra*-p-*anisylbutane*, small, coarse needles, m. p. 203° (decomp.). ββγγ-Tetrachloro-ααδδ-tetra-*p*-anisylbutane is reduced by zinc dust and boiling glacial acetic acid or, more slowly, by zinc dust and alcohol to the stereoisomeric βγ-*dichloro*-ααδδ-*tetra*-p-*anisyl*-Δ^{β}-*butenes*, colourless needles, m. p. 129—130° and lustrous leaflets, m. p. 182°, respectively; the corresponding tetrabromo-derivative, on the other hand, is reduced to ααδδ-tetra-*p*-anisyl-Δ^{β}-butinene, m. p. 110° (cf. Brand and Matsui, A., 1913, i, 1170). The stereoisomeric dichloro-compounds, m. p. 129—130° and 182°, respectively, are reduced by sodium and ethyl or amyl alcohol to ααδδ-*tetra*-p-*anisyl*-$\Delta^{\alpha\beta\gamma}$-*butatriene*, $C(C_6H_4{\cdot}OMe)_2{:}C{:}C{:}C(C_6H_4{\cdot}OMe)_2$, long yellow or orange needles, m. p. 242°, and a *substance*, $C_{32}H_{28}O_4$, red needles, m. p. 173°, to which, by analogy with the corresponding compound derived from dichlorotetraphenylbutene (this vol. i, 783), the formula $OMe{\cdot}C_6H_3{<}{\begin{matrix}C(C_6H_4{\cdot}OMe)\text{——}\\C[{:}C(C_6H_4{\cdot}OMe)]\end{matrix}}{>}CH$ is ascribed. The tetra-anisylbutatriene is oxidised by chromic acid in warm glacial acetic acid solution to carbon dioxide and *pp'*-dimethoxybenzophenone, m. p. 144°; it is reduced by sodium in boiling amyl alcoholic solution to ααδδ-tetra-*p*-anisylbutane, m. p. 116° (cf. Brand and Matsui, *loc. cit.*), and by hydrogen and palladised charcoal to tetra-*p*-anisylbutadiene (cf. Brand and Matsui, *loc. cit.*) or the butane compound. ααδδ-Tetra-*p*-anisyl-$\Delta^{\alpha\beta\gamma}$-butatriene is much more sensitive to light than the corresponding phenyl compound, and after comparatively short exposure becomes converted into a *substance*, $(C_{32}H_{28}O_4)_2$, greenish-yellow, strongly fluorescent crystals, m. p. 280°, and a smaller amount of a *product*, colourless needles, m. p. 286°, which has not yet been investigated further.

Reduction of βββ-trichloro-αα-di-*p*-phenetylethane by Devarda's

or Arndt's alloy gives a 2—3% yield of *pp'*-diethoxystilbene, m. p. 204—205°, together with small amounts of a substance, colourless needles, m. p. 146°, which is possibly dichlorotetraphenetylbutene, $C_{36}H_{38}O_4Cl_2$. Under similar conditions, *pp'*-diethoxystilbene is obtained from *ββ*β-*tribromo-αα-di-*p*-phenetylethane*, colourless needles, m. p. 119°; a compound, colourless needles, m. p. 180°, which is obtained simultaneously, may possibly be dibromotetraphenetylbutene. H. W.

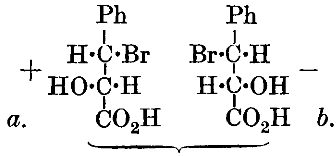
Semipinacolic and Semihydrobenzoinic Transpositions in the α-Phenyl-β-methylpropane-αβ-diol Series. Action of Dilute Acids on the Glycol and its Oxide; Elimination of HI from the Corresponding Iodohydrin. M. Tiffeneau and A. Orékhoff (*Bull. Soc. chim.*, 1921, [iv], **29**, 809—820).—A more detailed account of work already published (this vol., i, 243). W. G.

Semipinacolic and Semihydrobenzoinic Transpositions in the Phenyldimethylglycol Series. Action of Concentrated Acids. (Mlle) Jeanne Lévy (*Bull. Soc. chim.*, 1921, [iv], **29**, 820—829).—α-Phenyl-β-methylpropane-αβ-diol undergoes the semihydrobenzoinic transpositions with dilute acids, giving α-phenyl-α-methylpropaldehyde (cf. this vol., i, 243), but if concentrated acids are used the semipinacolic transposition, resulting in the formation of β-phenylbutanone, is produced. Thus dilute sulphuric acid and 50% oxalic acid produce the aldehyde, concentrated sulphuric acid gives the ketone, and phosphoric acid gives both the aldehyde and the ketone. Dimethylstyrene and its oxide behave in the same manner as the glycol in the presence of dilute and concentrated acids respectively. W. G.

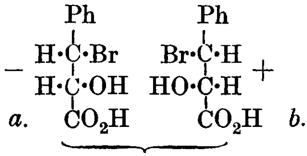
The Phenylalanine Series. I. Synthesis of *l*-3 : 4-Dihydroxyphenylalanine. E. Waser and M. Lewandowski (*Helv. Chim. Acta*, 1921, **4**, 657—666).—Contrary to the statements of Funk (T., 1912, **99**, 1004), tyrosine may be nitrated without racemisation, and aminotyrosine may be diazotised. *l*-3-*Nitrotyrosine*, $C_9H_{10}O_5N_2$, m. p. 222—224 (decomp.), $[\alpha]_D^{15}$ +3·21° (*hydrochloride*, radiate, yellow needles, m. p. 237°, decomp.), from *l*-tyrosine by nitration (Johnson and Kohmann, A., 1915, i, 899), on reduction (Funk, *loc. cit.*) yields *l*-3-*aminotyrosine*, needles, m. p. 287·5° (decomp.), $[\alpha]_D^{15}$ −3·61° [hydrochloride, prisms, m. p. 175° (decomp.)]. The orientation of these compounds follows from the conversion in excellent yield of the amino-derivative into *l*-3 : 4-dihydroxyalanine, identical in all respects with the natural product, by adding the diazotised solution to boiling copper sulphate solution. *l*-3 : 4-*Dihydroxyphenylalanine hydrochloride* forms rosettes of prismatic crystals, m. p. 209°, decomp. 220°. J. K.

Optically Active Bromohydroxy-β-phenylpropionic Acids. E. Berner and C. N. Riiber (*Ber.*, 1921, **54**, [*B*], 1945—1960; cf. A., 1917, i, 562).—The theoretically possible phenylbromo-

hydroxypropionic acids have been prepared and their relative configurations provisionally deduced. The following isomerides are possible.



(I.)



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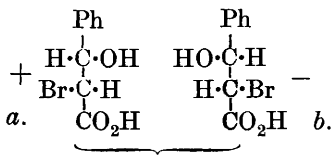

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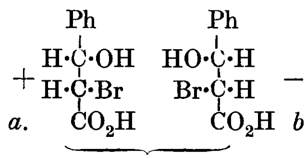
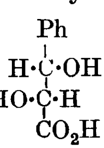


(IV.)

Phenylglyceric acid, m. p. 141°, is converted by aqueous hydrobromic acid solution, saturated at 0°, into *r*-β-bromo-α-hydroxy-β-phenylpropionic acid, monoclinic-prismatic or monoclinic-domatic crystals, $a:b:c=1{\cdot}822:1:0{\cdot}999$, $\beta=92°\ 42'$, *d* 1·676, m. p. 165°. Similarly, *d*-phenylglyceric acid, m. p. 164°, yields *d*-β-bromo-α-hydroxy-β-phenylpropionic acid (I*a*) whilst the *l*-acid (I*b*) is similarly prepared from the corresponding glyceric acid; the optically active acids, m. p. 143°, *d* 1·700, form monoclinic sphenoidal crystals, $a:b:c=1{\cdot}9862:1:0{\cdot}8564$. The *l*-acid has $[\alpha]_D^{20}$ −122·7°, $[\alpha]_C^{20}$ −95·3°, $[\alpha]_E^{20}$ −161·8° in 97·5 vol.% ethyl alcoholic solution (p=3·036) and $[\alpha]_D^{20}$ −114·92° (p=1·05); the specific rotation diminishes with increasing temperature. The *d*-acid has $[\alpha]_D^{20}$ +122·9° in ethyl alcohol (p=2·48) and $[\alpha]_D^{20}$ +116·0° in acetone. One hundred grams of chloroform dissolve 0·30, 1·00, and 1·00 gram of the *r*-, *d*-, and *l*-acids respectively at 20°. A 3% solution of the *r*-, *d*-, and *l*-acids in ethyl alcohol (99·80 vol. per cent.) has d_{20}^{20} 0·8047, 0·8046, and 0·8047 respectively. Reduction of the bromo-acids by means of sodium amalgam in acidified alcoholic solution gives the α-hydroxy-β-phenylpropionic acids; a change in the direction of rotation does not occur in the cases of the optically active acids. The configuration I*a* is assigned to the *d*-acid on account of its relationship to *d*-phenylglyceric acid, to which the annexed formula is assigned arbitrarily, the assumption being made that configurational change does not occur during the replacement of hydroxyl by bromine.



r-Phenylglyceric acid, m. p. 122°, is converted by hydrobromic acid solution into *r*-β-bromo-α-hydroxy-β-phenylpropionic acid, m. p. 157°, *d* 1·674, monoclinic-prismatic or monoclinic-domatic crystals, $a:b:c=1{\cdot}814:1:0{\cdot}976$, $\beta=93°\ 21'$. Similar treatment of the active phenylglyceric acids yields the optically active β-*bromo-α-hydroxy*-β-*phenylpropionic acids*, reaction being accompanied by change in the direction of rotation. The latter form monoclinic,

sphenoidal crystals, $a:b:c=1\cdot9840:1:0\cdot8543$, $\beta=94°\ 5'$, m. p. 138°; the *l*-acid has $[\alpha]_D^{20}$ −121·7°, $[\alpha]_C^{20}$ −94·2°, $[\alpha]_E^{20}$ −160·1° in ethyl alcohol (97·5 vol. %) and $[\alpha]_D^{20}$ −113·4° in acetone. The *d*-acid has $[\alpha]_D^{20}$ +122·3° ($p=2\cdot888$) and +117·6° ($p=1\cdot444$) in alcohol; the specific rotation diminishes with increasing temperature. One hundred grams of chloroform dissolve 0·20, 2·60, and 2·60 grams of the *r*-, *d*-, and *l*-acids respectively at 20°. The configuration II*b* is assigned to the *d*-acid, since, on reduction with sodium amalgam, it yields the same *d*-α-hydroxy-β-phenylpropionic acid as is obtained from the acid I*a*.

r-α-Bromo-β-hydroxy-β-phenylpropionic acid is prepared by boiling dibromocinnamic acid with water or by the addition of hypobromite to cinnamic acid. Under suitable condition, it can be isolated in two dimorphous forms, the α-modification, m. p. 125°, *d* 1·697, consisting of monoclinic crystals, $a:b:c=1\cdot0099:1:1\cdot1875$, $\beta=126°\ 45'$, whereas the β-*modification* forms rhombic crystals, *d* 1·691, $a:b:c=0\cdot7067:1:1\cdot2963$. The former modification is stable at the atmospheric temperature, whereas the latter is labile. The optically active acids are prepared by resolution of the *r*-acid by cinchonine (cf. Barkow, *Diss. Mannheim*, 1906) or by treatment of the active dibromosuccinic acids with water; contrary to the observations of Barkow (*loc. cit.*), the latter reaction occurs without change in the sign of rotation. The *d*-acid forms monoclinic-sphenoidal crystals, $a:b:c=0\cdot635:1:0\cdot697$, $\beta=104°\ 38'$, m. p. 119°, *d* 1·736; it has $[\alpha]_C^{20}$ +15·6°, $[\alpha]_D^{20}$ +20·2°, $[\alpha]_E^{20}$ +26·4°, $[\alpha]_F^{20}$ +32·4° ($p=3\cdot01$), and $[\alpha]_D^{20}$ +19·5° ($p=1\cdot53$) in ethyl alcohol (99·75 vol. %); the specific rotation increases with rise in temperature. The values, m. p. 116°, $[\alpha]_D^{20}$ −18·2°, in absolute alcohol were found for the *l*-acid. One hundred grams of chloroform dissolve 0·30, 0·66, and 0·37 gram of the *r*(α)-, *r*(β)-, and *d*-acids respectively at 20°. A 3% solution of the *r*-acid in alcohol has d_{20}^{20} 0·8047. Reduction of the α-bromo-β-hydroxy-β-phenylpropionic acids by sodium amalgam leads to the formation of the β-hydroxy-β-phenylpropionic acids, and is not accompanied by change in the direction of rotation in the cases of the optically active acids. Treatment of the *r*-acid, m. p. 125°, with hydrobromic acid gives dibromocinnamic acid, m. p. 195°, whereas the *d*-acid yields *d*-dibromocinnamic acid, m. p. 182°, $[\alpha]_D^{15}$ +45·8°, thus pointing to the configuration III*a* for the *d*-acid.

r-α-*Bromo*-β-*hydroxy*-β-*phenylpropionic acid*, m. p. 69° (formula group IV), cannot be prepared by the treatment of *allo*cinnamic acid dibromide with boiling water (which gives the stable acid, III, m. p. 125°), but results from the addition of hypobromite to potassium *allo*cinnamate solution; it forms rhombic, probably bipyramidal, crystals, $a:b:c=0\cdot6602:1:1\cdot2694$, *d* 1·724. The active *components* are produced by the resolution of the *r*-acid by means of strychnine in methylal solution and form monoclinic-sphenoidal crystals, $a:b:c=1\cdot1055:1:0\cdot8749$, $\beta=113°\ 2'$, m. p. 97°; the *l*-acid has $[\alpha]_C^{20}$ −8·25°, $[\alpha]_D^{20}$ −9·39°, $[\alpha]_E^{20}$ −10·44° in ethyl alcohol (99·80 vol. %) for $p=2\cdot30$ and $[\alpha]_D^{20}$ −13·06° ($p=0\cdot86$). The values, m. p. 93—94°, $[\alpha]_D^{20}$ +7·81°, in alcohol ($p=2\cdot31$) are

recorded for the *d*-acid. One hundred grams of chloroform dissolve 0·51 and 1·77 grams of the *r*- and *d*-acids respectively at 20°. A 3% solution of the *r*-acid in alcohol has d_{20}^{20} 0·8045. Reduction of the acids by sodium amalgam gives the β-hydroxy-β-phenylpropionic acids, the action being accompanied by a change in the direction of rotation in the cases of the optically active acids. Treatment of the *r*-acid, m. p. 69°, with hydrobromic acid gives cinnamic acid dibromide, m. p. 195°, in place of the expected *allo*-dibromide under similar conditions, the *l*-acid, m. p. 97°, yields a dextrorotatory mixture of cinnamic acid dibromides.

The methyl esters of the *r*-phenylglyceric acids, m. p. 141° and 122°, are converted by phosphorus pentabromide at a temperature not exceeding 80° into methyl dibromocinnamate, m. p. 117°. The dextrorotatory component of phenylglyceric acid, m. p. 141°, when esterified with diazomethane and treated with phosphorus pentabromide, yields methyl dibromocinnamate, m. p. 114°, $[\alpha]_D$ +22·9°; change of sign of rotation is not observed when the optically active dibromocinnamic acids are esterified with diazomethane. H. W.

The Fluorene Series. VI. A. SIEGLITZ and H. JASSOY (*Ber.*, 1921, **54**, [*B*], 2133—2138).—*Ethyl fluorene-9-glycollate*,

$$\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CH\cdot CH(OH)\cdot CO_2Et,$$

colourless rods, m. p. 81—82°, is obtained by the reduction of a solution of ethyl fluorene-9-glyoxylate in moist ether with aluminium amalgam and is transformed by boiling sodium ethoxide solution into *dibenzofulvene-ω-carboxylic acid*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!C\!:\!CH\cdot CO_2H$, yellow needles, m. p. 227—228° (decomp.), *methyl* ester, lustrous yellow needles, m. p. 112—113°, *ethyl* ester, which is more conveniently prepared from fluorenone, ethyl bromoacetate, and zinc in boiling benzene solution, b. p. 248°/13 mm., m. p. 77°. The unsaturated ester is reduced quantitatively to ethyl fluorene-9-acetate which, when treated with hydrazine hydrate in boiling alcoholic solution, gives the corresponding *hydrazide*, colourless needles, m. p. 188° (*benzylidene* derivative, colourless, slender needles, m. p. 192°). The latter is converted in the usual manner into the *azide*, decomp. 67—68°, and *urethane*, long, colourless needles, m. p. 112—113°. Conversion of the urethane into 9-aminomethylfluorene could not be effected with concentrated hydrochloric acid, sulphuric acid (50%), or concentrated ammonia; by distillation with lime, however, a reddish-yellow, unstable liquid, presumably the crude amine, was isolated, which rapidly loses ammonia when preserved in contact with air or treated with solvents, and yields a solid substance, (?) dibenzofulvene.

The following compounds are obtained by the reduction of the corresponding fulvenes with aluminium amalgam: 9-o-*methylbenzylfluorene*, colourless cubes, m. p. 71—72°; 9-p-*methylbenzylfluorene*, colourless crystals, m. p. 136—137°; 9:9′-m-*xylylenedifluorene*, needles, m. p. 119—120°; 9:9′-p-*xylylenedifluorene*,

colourless rods, m. p. 239—240°; 9-o-*chlorobenzylfluorene*, colourless leaflets, m. p. 67—68°; 9-m-*chlorobenzylfluorene*, colourless needles, m. p. 122—123°; 9-p-*chlorobenzylfluorene*, long, colourless spikes, m. p. 150—151°; 9-m-*bromobenzylfluorene*, colourless leaflets, m. p. 143—144°; 9-m-*iodobenzylfluorene*, feathery leaflets, m. p. 134—135°.

9-α-*Naphthylmethylfluorene*, colourless rods, m. p. 133—134°, and 9-β-*naphthylmethylfluorene*, m. p. 164°, are prepared from ethyl fluoreneglyoxylate and naphthylmethyl bromide. H. W.

The Fluorene Series. IV. Synthesis of *iso*Diphenic Acid. A. SIEGLITZ and J. SCHATZKES (*Ber.*, 1921, **54**, [*B*], 2070—2071).—It has been shown recently by Mayer and Freitag (this vol., i, 248) that Fittig's *iso*diphenic acid is diphenyl-2 : 3′-dicarboxylic acid. Its constitution is further confirmed by its production from fluorenone-3-carboxylic acid.

3-Methylfluorenone, m. p. 68°, is prepared from toluene, toluene-*p*-sulphonyl chloride, and anthranilic acid, and is oxidised by boiling potassium permanganate solution to *fluorenone*-3-*carboxylic acid*, yellow, crystalline aggregates, m. p. 285—286°; the latter is transformed by molten potassium hydroxide into *iso*diphenic acid, m. p. 213—214° after softening at 195° H. W.

Colophenic Acid. W. FAHRION (*Ber.*, 1921, **54**, [*B*], 1944).—In his recent publication (this vol., i, 512), Aschan appears to have overlooked the author's work on the autoxidation of colophony (A., 1907, i, 329). Aschan's colophenic acid is apparently identical with oxyabietic acid. H. W.

The Mechanism of the Action of Fused Alkalis. II. The Action of Fused Potassium Hydroxide on Phenylglyceric Acid. (The late) HENRY RONDEL LE SUEUR and CYRIL CHRISTIAN WOOD (T., 1921, **119**, 1697—1700).

ψ-Tetrahydroanemonic Acid. ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 679—691).—By warming ψ-tetrahydroanemonic acid (cf. *ibid.*, 1919, 739) with hydrogen iodide or by boiling tetrahydroanemonin with hydrogen iodide (*d* 1·7), *ψ-tetrahydroanemonic acid hydriodide*, $C_{10}H_{15}O_5I$, white prisms, m. p. 124°, is obtained; it is unstable and changes into ψ-tetrahydroanemonic acid when warmed with dilute alkali or boiled with water. On reduction with zinc and hydrochloric acid, the hydriodide produced an iodine-free acid, "*acetoneaceticvaleric*" [? *γ-keto-octane-αθ-dicarboxylic*] *acid*, $C_{10}H_{16}O_5$, white needles, m. p. 90° (*semicarbazone*, white prisms, m. p. 148°). From the semicarbazone, sebacic acid was isolated by Wolff's method of reduction (*Annalen*, 1866, **139**, 86). When heated with methyl alcohol and concentrated sulphuric acid, ψ-tetrahydroanemonin yields *methyl-ψ-tetrahydroanemonate*, a colourless oil, b. p. 184—185°/13 mm., produced also from ψ-tetrahydroanemonic acid by the same treatment; the ester yields ψ-tetra-

hydroanemonic acid on hydrolysis with cold alkali. ψ-Tetrahydroanemonic acid has probably one of the two formulæ

$$\begin{array}{l} CH_2\cdot C{:}CH\cdot CH_2\cdot CO_2H \\ \;|\qquad >O \\ CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot CO_2H \end{array} \quad \text{or} \quad \begin{array}{l} \qquad\;\; O\text{—}CO \\ CH_2\cdot C\cdot CH_2\cdot CH_2 \\ \;|\qquad >O \\ CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot CO_2H. \end{array}$$

K. K.

Constitution of the Peppermint Ketone of Eucalyptus Oils. L. GIVAUDAN & Co. (*Perf. Essent. Oil Rec.*, 1921, **12**, 80—81; cf. Smith and Penfold, *J. Roy. Soc. New South Wales*, 1920, **54**, 40).—Since by oxidation piperitone yields 2-hydroxy-Δ^1-menthen-3-one, it must have the constitution $CMe{<}\begin{matrix}CH\cdot CO-\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CHMe_2$.

CHEMICAL ABSTRACTS.

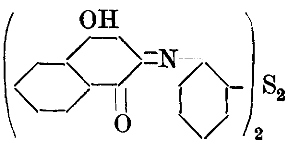
Reactivity of Doubly-conjugated Unsaturated Ketones. I. 4′-Dimethylamino-2-hydroxydistyryl Ketone. ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK (T., 1921, **119**, 1500—1515).

Reactivity of Doubly-conjugated Unsaturated Ketones. II. The Action of Hydroxylamine, Semicarbazide, and Phenylhydrazine on 4′-Dimethylamino-2-hydroxydistyryl Ketone and its Methyl Ether. ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK (T., 1921, **119**, 1515—1520).

Hydroxycarbonyl Compounds. VI. Phloroglucinol and Resorcinol Ketones. P. KARRER and S. ROSENFELD (*Helv. Chim. Acta*, 1921, **4**, 707—717; cf. this vol., i, 341).—An extension of previous work (A., 1919, i, 592). *Phloro*iso*butyrophenone*, m. p. 138—140°, forms a *dihydrate*, $C_6H_2(OH)_3\cdot CO\cdot CHMe_2,2H_2O$, m. p. 68°, and gives a brownish-red colour with ferric chloride. *Phloro*iso*valerophenone*, $C_6H_2(OH)_3\cdot CO\cdot CH_2\cdot CHMe_2$, m. p. 178°, *monohydrate*, m. p. 95°, colours ferric chloride brownish-red. *Phloro*iso*hexophenone*, $C_6H_2(OH)_3\cdot CO\cdot [CH]_2\cdot CHMe_2$, m. p. 122°, *monohydrate*, m. p. 104°, colours ferric chloride brownish-red. *Phloroenanthophenone*, $C_6H_2(OH)_3\cdot CO\cdot [CH_2]_4\cdot CH_2Me$, m. p. 107°, *monohydrate*, m. p. 98—100°. *Phloro-octophenone*, m. p. 124°, *monohydrate*, $C_6H_2(OH)_3\cdot CO\cdot [CH_2]_5\cdot CH_2Me,H_2O$, m. p. 106°. *Phlorostearophenone*, $C_6H_2(OH)_3\cdot CO\cdot [CH_2]_{15}\cdot CH_2Me$, m. p. 126—127°, colours ferric chloride brownish-red. *Resobutyrophenone*, $C_6H_3(OH)_2\cdot COPr$, m. p. 70°; *hemihydrate*, m. p. 51—52°. *Reso*iso*hexophenone*, $C_6H_3(OH)_2\cdot CO\cdot [CH_2]_2\cdot CHMe_2$, m. p. 83—84°, colours ferric chloride brownish-red. *Resoenanthophenone*, $C_6H_3(OH)_2\cdot CO\cdot [CH_2]_4\cdot CH_2Me$, m. p. 49°, *hemihydrate*, m. p. 43°, reacts similarly with ferric chloride. *Reso-octophenone*, $C_6H_3(OH)_2\cdot CO\cdot [CH_2]_5\cdot CH_2Me$, m. p. 59°, *hemihydrate*, m. p. 58°. *Methylphloro*iso*hexophenone*, $C_6HMe(OH)_3\cdot CO\cdot [CH_2]_2\cdot CHMe_2$, m. p. 156°. *Methylphloroenanthophenone*, $C_6HMe(OH)_3\cdot CO\cdot [CH_2]_4\cdot CH_2Me$, m. p. 143—144°, forms a monohydrate. *Methylphloro-octophenone*, $C_6HMe(OH)_3\cdot CO\cdot [CH_2]_5\cdot CH_2Me$, m. p. 135°, forms a monohydrate.

A comparative study of these compounds as remedies against the tape-worm showed that the resorcinol may replace the phloroglucinol residue, and that other acid residues are equally as effective as the butyryl and *iso*butyryl groups, the *iso*hexoyl residue being the most valuable. J. K.

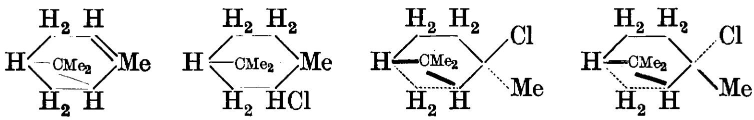
Action of o-Aminothiophenol on Orthoquinones. III. KNUT STAHRFOSS (*Helv. Chim. Acta*, 1921, **4**, 644—657).—Besides the two products of the condensation of *o*-aminothiophenol and 4-amino-β-naphthaquinone in presence of acetic acid already described (this vol., i, 457), a third is obtained as a sparingly soluble potassium salt by extraction of the precipitate resulting from the dilution of the acetic acid solution, with boiling 3% potassium hydroxide solution. The new compound forms brown needles, and is shown to be the *disulphide* (annexed formula) corresponding with *o-thiolphenyl-4-hydroxy-β-naphthaquinone-2-imide*. This formula is confirmed by syntheses of the compound from *o*-aminothiophenol and 4-hydroxy-β-naphthaquinone and from 2 : 2′-diaminodiphenyl disulphide and 2-amino-α-naphthaquinone. It cannot be obtained from β-naphthaquinone-4-sulphonic acid (cf. Böniger, A., 1894, i, 199) or from 4-amino-β-naphthaquinone. It is therefore formed in the above condensation by a preliminary reaction corresponding with the formation of *o*-hydroxyanilino-α-naphthaquinone (Kehrmann, A., 1895, i, 245) from *o*-aminophenol and 4-hydroxy-β-naphthaquinone, followed by replacement of an amino- by a hydroxyl-group (D.R.P. 97675) and oxidation of the thiophenolic group at the expense of the aminoquinone. The formula also explains the salt-formation, and the fact that the compound does not condense with *o*-aminophenol or *o*-phenylenediamine. J. K.



o-Dimethylanthraquinones and their Derivatives. ARTHUR FAIRBOURNE (T., 1921, **119**, 1573—1582).

2-Aldehydoanthraquinone. WERNER JACOB (*Helv. Chim. Acta,* 1921, **4**, 782—788).—Condensation products of 2-aldehydoanthraquinone (*p-nitrophenylhydrazone*, $C_{21}H_{13}O_4N_3$, leaflets, m. p. 305—306°) with compounds containing a reactive methylene group have been prepared as follows : with acetophenone, $C_{23}H_{14}O_3$, needles, m. p. 241—242° ; with 1-hydroxy-2-methyl ketone, $C_{27}H_{16}O_4$, reddish-yellow needles, m. p. 296—297° (*methyl ether*, $C_{28}H_{18}O_4$, yellow leaflets, m. p. 214—215°) ; with 1-hydroxy-4-naphthyl methyl ketone, $C_{27}H_{16}O_4$, yellow needles, m. p. 226—227° (*methyl ether*, $C_{28}H_{18}O_4$, yellow needles, m. p. 228—229°) ; with coumaranone, $C_{23}H_{12}O_4$, yellow needles, m. p. 309—310° ; with 6-methoxycoumaranone, $C_{24}H_{14}O_5$, yellow needles, m. p. 280—282° ; with α-naphthacoumaranone, $C_{27}H_{14}O_4$, yellow needles, m. p. 223—225° ; with 5-bromoindanone, $C_{24}H_{13}O_3Br$, yellowish-green leaflets, m. p. 299—300° ; with indandione, $C_{24}H_{12}O_4$, greenish-yellow needles, m. p. 300—301°. J. K.

tert.-Pinene Hydrochloride. The Pinacolin Transformation. Ossian Aschan (*Öfvers. Finska Vet.-Soc.*, 1914, **57**, [*A*], No. 1, 35 pp.; from *Chem. Zentr.*, 1921, iii, 629—631).—The action of dry hydrogen chloride on pinene (I) at low temperatures does not give ordinary pinene hydrochloride (bornyl chloride) (II), but an isomeric liquid compound, tert.-*pinene hydrochloride* (III). This compound differs from bornyl chloride in that it contains the bicyclic tetrocean system of pinene and decomposes partly on treatment with aniline, giving hydrogen chlorides and a pinene which is optically active in the same sense as the original material. The elimination of hydrogen chloride takes place with development of heat, *tert.*-pinene hydrochloride being stable only below $-10°$. In the absence of cooling, the temperature rises to 60—80° with transformation into solid bornyl chloride (II).



(I.) (II.) (III.) (IV.)

It is supposed that in the formation of bornyl chloride from pinene and hydrochloric acid (pinacolin transformation) the unstable compound (III) occurs as an intermediate product.

Nopinene forms with hydrogen chloride the same tertiary pinene hydrochloride (III) as is given by ordinary pinene with aniline. The change from nopinene to ordinary pinene by way of the compound III takes place more directly and simply than the change by way of nopinic acid $\longrightarrow$ nopinone $\longrightarrow$ nopinolacetic acid (Wallach, A., 1909, i, 706). No verifiable amount of nopinene is formed in the decomposition above mentioned. The compound, $C_{10}H_{17}Cl$, obtained by Wallach by the action of phosphorus pentachloride on methyl nopinol is probably a stereoisomeride of the compound III and may have the constitution represented by formula IV. (The thick lines are supposed to be above and the dotted lines below the plane of the paper in formulæ III and IV). The rate of transformation of tertiary pinene hydrochloride is greater than its rate of formation from pinene and hydrogen chloride above 0°, and even at low temperatures it cannot be obtained free from bornyl chloride. It has a suffocating odour and attacks the mucous membrane strongly. The saturation of the original hydrocarbon with dry hydrogen chloride was carried out at $-15°$ with the addition of 4 to 10% of ether. On adding to the hydrochloride an equal volume of aniline and leaving it at the ordinary temperature, the transformation sets in quickly and the temperature of the mixture rises above 80°. When the temperature falls again the mixture is heated for about four hours on a water-bath. Glacial acetic acid is added to fix the excess of aniline and volatile products are removed by steam distillation. The principal product is bornyl chloride. The mixture of hydrocarbons resulting from its decomposition consists essentially of ordinary pinene, but contains

some dipentane and limonene. The fraction distilling over between 162° and 167° appears to contain an unknown bicyclic terpene. Using pinene from different sources with varying optical rotations, different results were obtained both for the yield of bornyl chloride and of regenerated pinene. G. W. R.

Conversion of Pinene Compounds into a Mixture of *iso*-Bornyl Ester and Camphene. L. G. WESSON (U.S. Pat. 1372382).—Pinene hydrochloride is mixed with glacial acetic acid in the proportions of 100 to 300 parts, a small quantity of rather coarse zinc powder (preferably about 2 parts) is added after the mixture has been heated to vigorous boiling under a reflux condenser, and the boiling is continued for about eighteen hours. The zinc slowly dissolves and a large proportion of the hydrogen chloride is evolved and recovered. After about eighteen hours, the mixture usually contains about 83—85 parts of *iso*bornyl acetate, 10 parts of camphene, 5 parts of camphene hydrochloride, and 10 parts or less of unconverted pinene hydrochloride. A mixture of *iso*bornyl acetate, camphene, and camphene hydrochloride is separated by fractional distillation in a vacuum and this mixture may be employed for the production of synthetic camphor. The use of such a small amount of zinc and the avoidance of unduly high temperatures or more prolonged heating obviate the formation of any considerable quantity of resinous substances. Instead of acetic acid, formic, propionic, stearic, benzoic, or salicylic acid or other acid may be used and instead of pinene hydrochloride the hydrobromide or hydrofluoride is suitable for carrying out similar reactions. CHEMICAL ABSTRACTS.

Pinene. IV. Synthesis of Pinocamphone and α-Pinene from Monocyclic Compounds. L. RUZICKA and H. TREBLER (*Helv. Chim. Acta*, 1921, **4**, 666—678; cf. this vol., i, 573).—By condensation of ethyl *r*-pinate with ethyl chloroacetate in presence of sodium ethoxide (Darzens, A., 1905, i, 116) or, much less effectively, of sodamide (Claisen, A., 1905, i, 286), the *glycidic ester*, $C_{16}H_{26}O_5$, b. p. 140—150°/0·3 mm., is obtained. The corresponding *acid*, $CO_2H{\cdot}CH_2{\cdot}CH{<}{\substack{CMe_2\\ CH_2}}{>}CH{\cdot}CMe{<}{\substack{CH{\cdot}CO_2H,\\ |\\ O}}$ m. p. 128° (decomp.), is converted at 230° in a vacuum into the *semialdehyde* of *homopinocamphoric acid*, $CO_2H{\cdot}CH_2{\cdot}CH{<}{\substack{CMe_2\\ CH_2}}{>}CH{\cdot}CHMe{\cdot}CHO$, b. p. 130—140°/0·3 mm. [*semicarbazone*, $C_{12}H_{21}O_3N_3$, m. p. 193—195° (decomp.)], from which *homopinocamphoric acid*,

$$CO_2H{\cdot}CH_2{\cdot}CH{<}{\substack{CMe_2\\ CH_2}}{>}CH{\cdot}CHMe{\cdot}CO_2H,$$

is obtained, and converted through its silver salt into its *diethyl* ester, $C_{15}H_{26}O_4$, b. p. 130°/1 mm., 120°/0·2 mm. *r*-Pinocamphone, identical with that derived from pinene, is best obtained from homopinocamphoric acid by subjecting its diethyl ester to the Dieckmann reaction, and hydrolysing the product with acid, much less satisfactorily by heating the acid with acetic anhydride (Blanc,

A., 1907, i, 710), and not at all by distillation of the lead salt. The conversion of the ketone into α-pinene has already been achieved (this vol., *loc. cit.*; Tschugaev, A., 1908, i, 93). The expansion of this partial into a total synthesis is discussed. J. K.

Chemistry of the Terpenes. XX. The Action of Hypochlorous Acid on Pinene. GEORGE GERALD HENDERSON and JOSEPH KENNETH MARSH (T., 1921, **119**, 1492—1500).

The Olibanols. EMIL FROMM and RICHARD KLEIN (*Annalen*, 1921, **425**, 208—216).—Pure pinene when oxidised by cold permanganate gives pinonic acid (isolated as its *semicarbazone*, m. p. 204°), but no pinononic acid, the production of which by Wagner and Erschtschikowski (A., 1896, i, 380) must be attributed to the presence of verbinone or some analogous substance in the pinene they employed. Olibanol (Fromm and Autin, A., 1914, i, 70), when isolated from oil of frankincense by distillation in a vacuum, has b. p. 117—119°/22 mm., and also yields no pinononic acid. It is called *α-olibanol* to distinguish it from the isomeride, *β-olibanol*, into which it is converted on distillation at atmospheric pressure (b. p. 210—211°), which yields pinononic acid on oxidation. α-Olibanol, on reduction by sodium and alcohol, gives *dihydro-olibanol*, $C_{10}H_{18}O$, b. p. 100—102°/25 mm., which has an odour resembling sage and appears to be an alcohol. It was characterised by a crystalline o-*nitrobenzoate*, m. p. 135—137°. β-Olibanol does not show these properties. Another isomeride, *γ-olibanol*, b. p. 114—116°/15 mm., d^{18}=0·9502, isolated from a different specimen of oil of frankincense, gives no dihydro-compound, and does not yield β-olibanol on distillation. On oxidation, it gives a liquid acid from which no semicarbazone can be obtained. C. K. I.

Physical Constants and Characteristic Derivatives of the Principal Constituents of the Essential Oils. (*Roure-Bertrand fils Sci. Ind. Bull.*, 1920, [4], No. 2, 37—48).—A table is given showing the physical constants and characteristic derivatives of the principal aldehydes found in essential oils, namely: aromadendral, myrtenal, dihydrocuminaldehyde, citral, neral, phellandral, citronellal, *nor*-tricycloekasantalal, santalal, farnesal; formaldehyde, acetaldehyde, butaldehyde, valeraldehyde, *iso*valeraldehyde, *n*-hexaldehyde, *n*-octaldehyde, *n*-nonaldehyde, decaldehyde, lauraldehyde, benzaldehyde, phenylacetaldehyde, cumaldehyde, cinnamaldehyde, salicylaldehyde, anisaldehyde, *o*-methoxycinnamaldehyde, *p*-methoxycinnamaldehyde, vanillin, piperonaldehyde, furfuraldehyde, and 2-methylfurfuraldehyde. CHEMICAL ABSTRACTS.

The Essential Oil from *Andropogon iwarancusa*, Jones, and the Constitution of Piperitone. JOHN LIONEL SIMONSEN (T., 1921, **119**, 1644—1654).

Certain Essential Oils. (*Roure-Bertrand Fils Sci. Ind. Bull.*, 1920, [4], No. 2, 29—37).—Oil of chenopodium: By steam distillation, 0·7% of a light-yellow oil was obtained from chenopodium seed obtained from the Dutch East Indies. Its analytical constants

are: d^{15} 0·9763; $[\alpha]_D^{15}$ ±0°; acid number 0·93; saponification number 7·47; ester number 6·54; solubility in 70% alcohol, 2 vols. and over. By extracting the distilled waters with light petroleum, an additional 0·35% of oil was obtained possessing the following characters: d^{15} 0·9843; $[\alpha]_D^{15}$±0°; acid number 0·93; saponification number 13·98; ester number 13·05; soluble with difficulty in 70% alcohol. The optical rotation of these oils differentiates them from the American oil which has $[\alpha]_D$ −4° to −3° 30′. Oil of *Skimmia laureola:* A sample of oil distilled from the herb of *Skimmia laureola,* Hook showed: d^{18} 0·8931; $[\alpha]_D^{18}$+4° 28′; acid number 0; saponification number 82·13; soluble in 3 volumes of 90% alcohol. Oil of cinnamon from Annam: a sample gave: d^{15} 1·051; n_D 1·6090; $[\alpha]_D$−0° 8′; acid number 2·8; aldehyde content 95%; solubility in 70% alcohol, one volume and over. The odour of the oil is more pungent and less fine than that of oil of Ceylon cinnamon. It resembles a rectified Chinese oil of good quality in its characters.

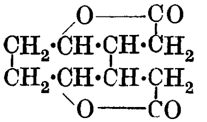
CHEMICAL ABSTRACTS.

Labdanum and the Analytical Characters of the Oils of *Cistus Ladaniferus,* L., and *Cistus monspeliensis,* L. (*Roure-Bertrand Fils Sci. Ind. Bull.*, 1920, [4], No. 2, 25—29).—Analytical data obtained by Pelletier and by Guibourt for labdanum are given, also data of a similar nature by Parry ("Chemistry of Essential Oils," vol. 1, p. 503) and Masson (A., 1912, i, 280) for the oil distilled from the oleoresin. The author obtained 0·06% of a golden-yellow oil by steam distillation from the oleoresin extracted from *Cistus ladaniferus* L. This oil possessed the following characters: d^{20} 0·9033; $[\alpha]_D^{17}$−12° 10′; $n_D^{12\cdot5}$ 1·4800; acid number 3·7; saponification number 22·37; ester number 18·67; solubility in 90% alcohol 0·5 to 5 volumes. The extraction of the distilled waters with light petroleum yielded an additional 0·02% of oil with the following characters: $d^{17\cdot5}$ 0·9755; $[\alpha]_D^{17}$ −2° 40′; acid number 18·67; saponification number 41·07; ester number 22·40; solubility in 90% alcohol 0·5 vol. and over. Data obtained by Schimmel and Co., (*Semi-Ann. Rept.*, 1903, October, p. 81) for the oil obtained from *Cistus monspeliensis* are also given. CHEMICAL ABSTRACTS.

Presence of Manganese in Raw Caoutchouc and the Origin of Tackiness. G. BRUNI and C. PELIZZOLA (*Atti R. Accad. Lincei*, 1921, [v], **30**, ii, 37—41).—When kept at the ordinary temperature, a mixture of caoutchouc with 1% of colloidal manganese dioxide very soon becomes tacky and in a few weeks almost liquid. The number of milligrams of manganese per 100 grams of caoutchouc has been found to vary from 0·0625 to 0·250 with the sound material, from 3·75 to 20 for samples showing uniform and profound tackiness, and from 0·625 to 3·75 for slightly and irregularly tacky samples. The manganese probably causes catalytic oxidation of the caoutchouc. T. H. P.

Anemonin Derivatives. YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 331—335; cf. A., 1920, i, 70, 321, 493, 678; this vol., i, 792).—When reduced with sodium amalgam

and acetic acid at the ordinary temperature, anemonin yields mainly dihydroanemonin and a small quantity of a substance having m. p. 98°, whilst the latter only is produced by using boiling methyl alcohol as solvent. When heated with hydriodic acid, the substance, m. p. 98°, yields anemonolic acid, and therefore is proved to be dimethyl anemonolate. iso*Tetrahydroanemonin*, m. p. 142°, is produced by reducing anemonin with sodium amalgam and acetic acid in boiling alcohol or from dihydroanemonin by the same



method, and from its resemblance to α-angelica lactone and dihydroanemonin the annexed formula is assigned to it. By heating anemonin dihydrobromide, $C_{10}H_8O_4,2HBr$, m. p. 182°, with anhydrous sodium acetate in glacial acetic acid solution on the water-bath, anemonin itself is reproduced, the tetramethylene ring is therefore preserved in the derived substance. By reducing furan-2 : 5-dipropionic acid with hydrogen in the presence of platinum black, sebacic acid is produced together with a small quantity of a substance crystallising in prisms, m. p. 113°, probably *tetrahydrofuran-2 : 5-dipropionic acid.* Dihydroanemonin condenses with benzaldehyde and furfuraldehyde, producing *dibenzylidenedihydroanemonin*, colourless scales, m. p. 225°, and *difurfurylidenedihydroanemonin*, dark yellow scales, m. p. 222° respectively. *Anisylidenetetrahydroanemonic acid*, yellow scales, m. p. 160°, is produced by adding anisaldehyde to an alkaline solution of tetrahydroanemonic acid.

K. K.

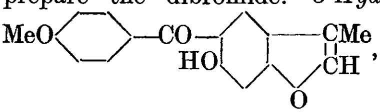
Tannins and Similar Substances. VIII. The Tannin of the Edible Chestnut. KARL FREUDENBERG and HANS WALPUSKI (*Ber.*, 1921, **54**, [*B*], 1695—1700; cf. this vol., i, 576).—The isolation of the crude tannin from the wood is described in detail, the total yield being more than 5% of the initial material. The composite nature of the product is deduced from the fact that hydrolysis with dilute sulphuric acid gives a little quercetin, traces of gallic acid, 2% of sugar (chiefly dextrose), and 15—20% of ellagic acid, all of which are present in the combined form; simultaneously, however, the tannin is itself extensively decomposed. The action of emulsin does not lead to the separation of dextrose or of ellagic acid; the latter therefore does not appear to be present in the form of a glucoside and this hypothesis is confirmed further by the stability of its compound towards cold dilute alkali. On the other hand, Aspergillus-tannase caused a slow separation of ellagic acid when used in relatively large amount and finally gives a product from which dilute sulphuric acid does not liberate more than 3% of the acid; simultaneously, the quercetin component is hydrolysed, whilst traces of gallic acid and small amounts of sugar, chiefly dextrose, are obtained. The purified tannin is a yellowish-red substance which forms more than half of the original crude product. It shows the usual tannin reactions. It gives a blue coloration with iron salts, but does not yield a precipitate with bromine water. It is not further affected by tannase, and is not decomposed into

simpler constituents by other hydrolysing agents. It does not appear to belong to the class of ester tannins or of catechins, since it does not contain phloroglucinol, is strongly acidic, and almost insoluble in ethyl acetate. The acidity indicates a molecular weight of about 400 or some multiple thereof.

Chestnut tannin appears, therefore, to be a representative of a new type of tannin and to be very closely allied to that of the native oak (Freudenberg, *Naturwiss.*, 1920, **8**, 905), with regard to which the investigation is to be pursued. H. W.

Syntheses in the Bergapten Group and of Other Hydroxycoumarone Derivatives. P. KARRER, A. RÜDLINGER, A. GLATTFELDER, and L. WAITZ (*Helv. Chim. Acta*, 1921, **4**, 718—728).—Since the failure to obtain a coumarin derivative, from 5-hydroxy-2-methylcoumarone-4-acrylic acid (A., 1920, i, 627) might possibly have been due to the situation of the unsaturated side chain in the 3- instead of the 4- position, 5-hydroxy-4-aldehydo-2 : 3-dimethylcoumarone has been synthesised from orcinol, and found also not to furnish a coumarin derivative. The formula for bergapten (Thoms, A., 1912, i, 40) therefore loses in probability.

5-*Hydroxy*-2 : 3-*dimethylcoumarilic acid*, $C_{11}H_{10}O_4$, m. p. 215—220°, from the ester (Kostanecki and Tambor, A., 1909, i, 319), is converted by distillation into 5-*hydroxy*-2 : 3-*dimethylcoumarone*, $OH\cdot C_6H_2Me<\substack{CMe\\O\text{——}}>CH$, m. p. 102°, from which the 4-*aldehydo*-derivative, $C_{11}H_{10}O_3$, needles, m. p. 210°, is prepared by treatment with hydrocyanic acid and zinc chloride. *Aldehydophloroglucinol monomethyl ether*, $C_8H_8O_4$, of uncertain orientation, from phloroglucinol monomethyl ether, yields 7-(or 5-)*acetoxy*-5-(or -7-)*methoxycoumarin*, $OAc\cdot C_6H_2(OMe)\Big<\begin{matrix}CH:CH\\ O\text{—}CO\end{matrix}$, leaflets, m. p. 136—137°, of which the nucleus is attacked when the attempt is made to prepare the dibromide. 5-*Hydroxy*-4′-*methoxy*-2-*methyldepsenone*,



yellow needles, m. p. 178°, from 5-hydroxy-2-methylcoumarone by the Hoesch reaction, is reduced to 5-*hydroxy*-4′-*methoxy*-2-*methyldepsenol*, $C_{17}H_{16}O_4$, m. p. 117°. The syntheses of 5 : 4′-*dihydroxy*-2-*methyldepsenone*, $C_{16}H_{12}O_4$, yellow needles, m. p. 298°, and of 5 : 3′ : 4′-*trihydroxy*-2-*methyldepsenone*, $C_{16}H_{12}O_5$, m. p. 250°, by the Hoesch reaction must be carried out at 80—90°. 5 : 4′-*Dihydroxy*-2-*methyldepsenol*, $C_{16}H_{14}O_4$, is readily oxidised by the air. J. K.

A New Type of Iodine Compound. JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY (T., 1921, **119**, 1550—1554).

The Structural Relation of *iso*Quinoline- and Phenanthrene-Alkaloids. INGO W. D. HACKH (*Chem. News*, 1921, **123**, 178—179).—The use of structure symbols (A., 1919, i, 245) reveals an interesting structural relationship amongst alkaloids containing

the *iso*quinoline nucleus. Alkaloids such as morphine, berberine, papaverine, glaucine, narcotine, corydaline, dicentrine, protopine, cryptopine, etc., appear to belong to different groups when the usual structural formulæ are used, but when these structural formulæ, or the corresponding structure symbols, are turned so that the *iso*quinoline nucleus occupies the same relative position in each, a structural relationship, which genetically connects all these alkaloids, may be traced, and the alkaloids may be classified, thus :

Laudosine
Papaverine
Paperoline, etc.

↙ ↓ ↘ ↘

Corydine, Corytuberine, Glaucine, etc. → (↙) Morphine, Codeine, Dionine, Thebaine, etc.; (↓) Dicentrine, Bulbocapnine, etc.

? → Hydrastine, Narcotine, etc.

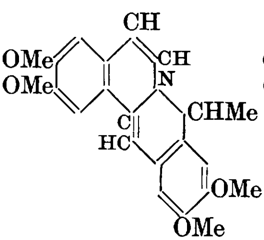
? → Cryptopine, etc. → Protopine, etc.

Corydaline, etc. → Berberine, Canadine, Artarine, etc.

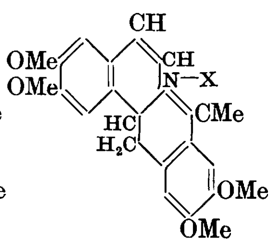
On this basis, Pschorr's formula for morphine is regarded as more probable than the formula of Freund and others. F. M. R.

Chelerythrine. P. KARRER (*Helv. Chim. Acta*, 1921, **4**, 703—706).—Replying to criticisms by Gadamer (A., 1920, i, 872), the author claims to have been the first to point out the analogy of chelerythrine with cotarnine (A., 1917, i, 349), and maintains his view that the basic properties are due, not to the nitrogen atom, but to another group, possibly the carbonyl group. The composition of methylchelalbine, $C_{17}H_{15}O_3N$, m. p. 204°, and the melting points of chelerythrine cyanide (248—249°) and phenylhydrazone (158—160°) are confirmed, but dihydrochelerythrine is now found to melt at 162—163°. J. K.

Reduction of Coralyne to Dihydrocoralyne and α-Coralydine. WILHELM SCHNEIDER and OTTO BÖGER (*Ber.*, 1921, **54**, [*B*], 2021—2031).—It has been shown previously (Schneider and Schroeter, A., 1920, i, 760) that coralyne, obtained by the action of acetic anhydride in the presence of sulphoacetic acid on papaverine, is a hexadehydrocoralydine. It is therefore to be expected that it would be reduced to coralydine, and this is shown to be the case, the α-modification of the base (cf. Pictet, A., 1913, i, 1224) being produced. Hydrogenation is, however, never complete, and dihydrocoralyne is always formed to a greater or less extent; since the base itself is



(I.)



(II.)

intensely yellow whereas the salts are colourless, the annexed formulæ I and II are proposed for these compounds.

Coralyne sulphoacetate, $C_{22}H_{22}O_4N{\cdot}SO_3{\cdot}CH_2{\cdot}CO_2H,H_2O$, is reduced by zinc and sulphuric acid in boiling glacial acetic acid solution to a mixture of α-coralydine and dihydrocoralyne, the relative proportions of which depend largely on the type of zinc used; the mixed bases are converted into their iodides and subsequently, for purposes of separation, into the chlorides. The following salts of α-coralydine are described, the melting points as recorded by Pictet (*loc. cit.*) being enclosed within brackets: hydrochloride, colourless, slender rods, m. p. 255° (254°); *hydriodide*, minute, pointed needles, m. p. 242—243°; nitrate, m. p. 240—245° after incipient decomposition at about 150° (242°); platinichloride, a yellow powder, decomp. 230° (246—247°); aurichloride, a red, crystalline powder, m. p. 139° (154)°; picrate, large, yellow needles, m. p. 139—140° (134°). α-Coralydine has m. p. 148°, in agreement with Pictet's observations, and is converted by iodine and alcohol into dehydrocoralydine iodide, m. p. 264·5° (264°). It is remarkable that β-coralydine does not appear to be formed.

Dihydrocoralyne, slender, yellow needles, m. p. 200°, is obtained by the rapid crystallisation from alcohol of the base, precipitated from its salts by ammonia; the moist base is extremely sensitive to atmospheric oxidation, by which it is converted into a *substance*, red needles, m. p. 241°, which has not yet been investigated completely. When boiled with water free from carbon dioxide, the *iso*-base is partly transformed into the ammonium hydroxide base, but slowly reverts to its original form when the solution is cooled. It is converted by iodine and alcohol into coralyne iodide, m. p. 278°. The following salts are described; *chloride* ($+6H_2O$), pale yellow, silky, crystalline aggregates, m. p. about 95° after softening at 85°, anhydrous, m. p. 194°; *iodide*, almost colourless, prismatic rods, m. p. 234°; *hydrogen sulphate* ($+H_2O$), m. p. 277°; *nitrate* (+aq), m. p. above 85°; *platinichloride*, a yellow powder, decomp. 263° after blackening above 150°; *aurichloride*, m. p. 110—115° (decomp.), and after re-solidification, decomp. above 260° after darkening at about 170°; *picrate*, m. p. about 237°.

H. W.

Harmine and Harmaline. V. The Synthesis of Norharman. WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (T., 1921, **119**, 1602—1642).

The Alkaloids of the Lobelia Plant. I. HEINRICH WIELAND (*Ber.*, 1921, **54**, [*B*], 1784—1788).—The isolation of two crystalline alkaloids, lobeline and lobelidine, from *Lobelia inflata* of North America is described. The former, $C_{23}H_{29}O_2N$, is a colourless, crystalline, monacid base which yields neutral salts. It does not appear to contain a ketonic or hydroxy-group and its stability towards alkali indicates the absence of the lactone group. A methoxyl radicle is not present. The nitrogen atom appears to be tertiary. Its most remarkable characteristic is the readiness

with which it yields acetophenone when warmed with water, but the fate of the remainder of the molecule has not yet been elucidated.

The isolation of lobeline from the crude mixture of bases depends on the observation that its hydrochloride can be removed from aqueous solution by repeated agitation of the latter with chloroform; the final purification is effected by crystallisation from benzene, alcohol, or ether. *Lobeline* crystallises in broad, colourless needles, m. p. 130—131°, $[\alpha]_D^{15°} -42·85°$, in alcoholic solution. The *sulphate, nitrate, bromide,* and *chloride* are placed in order of increasing solubility in water; the *platinichloride* and *mercuric chloride* compound are amorphous.

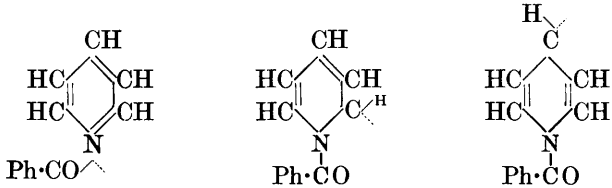
Lobelidine, $C_{20}H_{25}O_2N$, small, irregular prisms, m. p. 106°, is isolated from the final ethereal mother-liquors obtained during the preparation of lobeline. Its *hydrochloride*, matted needles, has m. p. 165° after darkening at about 160°. H. W.

Acetyl-*N*-methyl*iso*papaverine. WILHELM SCHNEIDER and ARNOLD KÖHLER (*Ber.*, 1921, **54**, [*B*], 2031—2033).—The conception of ψ-coralyne as a derivative of papaverine (cf. Schneider and Schroeter, A., 1920, i, 760) is confirmed further by the observation that its methiodide is converted by treatment with alkali into *acetyl*-N-*methyl*iso*papaverine*, yellow needles, m. p. 191° (*phenylhydrazone*, long, slender needles, m. p. 236·5°), which is readily reconverted by hydriodic acid into the original methiodide; the *iso*-base shows little tendency to pass into the ammonium form. Attempts to isolate an intermediately formed red, crystalline product (which is possibly analogous with the pyranhydrones of Schneider and Meyer, this vol., i, 680) were unsuccessful. H. W.

Preparation of a Derivative of Thebaine. EDMUND SPEYER, ELSE FREUND, WALTER FREUND, HELMUTH FREUND, and LISELOTTE FREUND (D.R.P. 338147; from *Chem. Zentr.*, 1921, iv, 422).—Thebaine in aqueous-alcoholic solution is treated with excess of molecular hydrogen, using colloidal metallic catalysts of the platinum group. For example, to a cooled solution of thebaine in 96% ethyl alcohol equal quantities of water and a palladium sol (1 c.c.= 0·0025 gram of Pd) are added, and the mixture is shaken in an atmosphere of hydrogen until no further absorption takes place. The palladium is then precipitated and the ethyl alcohol distilled off. After addition of aqueous ammonia, the residue is extracted with chloroform. The oil remaining after evaporation of the chloroform solution is triturated with ethyl alcohol and a *hydrochloride*, $C_{18}H_{23}O_3N,HCl$, prepared by the action of hydrochloric acid in alcoholic solution; it forms crystals, m. p. 310° (decomp.). The free *base*, $C_{18}H_{23}O_3N$, crystallises in leaflets (from alcohol) and has m. p. 145—150°. It is precipitated from solutions of its salts by excess of sodium carbonate or ammonia. With excess of alkali the precipitate of the base is redissolved; it is thus amphoteric in character. In these properties and in its stability in the presence of mineral acids, the compound described differs from tetrahydrothebaine, $C_{19}H_{25}O_3N$ (Oldenberg, A., 1913, i, 1093; Braun, A.,

1914, i, 1138). It contains one methoxyl group and has the characters of a ketone. G. W. R.

The Free Ammonium Radicle. I. Benzoylpyridinium. ERNST WEITZ, ADOLF ROTH, and ANNEMARIE NELKEN (*Annalen*, 1921, **425**, 161—186).—When zinc dust acts on a mixture of benzoyl chloride and pyridine the product, brown leaflets, m. p. 229° (decomp.), has the composition $C_{12}H_{10}ON = C_5H_5NBz$, and must therefore be represented by a formula containing either tervalent carbon or quadrivalent nitrogen. The formula I is regarded as most probable, but the substance is considered capable of reacting in the forms of its " valency-isomerides " II and III. It is termed 1-*benzoylpyridinium.*



(I.) (II.) (III.)

It has the normal molecular weight in boiling ethylene dibromide and in boiling chlorobenzene, but is associated in naphthalene at the freezing point.

When solutions of 1-benzoylpyridinium are shaken with air they are decolorised, half an atomic proportion of oxygen being absorbed. If they are titrated with halogens until colourless, one atom of halogen is taken up. In each case the principal products are benzoic acid and 4 : 4′-dipyridyl, the formation of which is most easily explicable on the assumption that the valency isomeride (III) takes part in the reaction. 1-Benzoylpyridinium is not a base.

4 : 4′-*Dipyridyl monobenzoate* crystallises in leaflets, m. p. 108°, and the *dibenzoate* in leaflets, m. p. 116°. C. K. I.

The Free Ammonium Radicle. II. Benzylpyridinium. ERNST WEITZ and ANNEMARIE NELKEN [with R. LUDWIG] (*Annalen*, 1921, **425**, 187—207; cf. preceding abstract).—1 : 1′-Dibenzyltetrahydro-4 : 4′-dipyridyl, which was obtained by Hofmann (A., 1881, 921) and reinvestigated by Emmert (A., 1919, i, 455), has been shown by the latter (A., 1920, i, 331) to undergo dissociation in solution, forming a coloured C_{12}-compound, which may be called 1-*benzylpyridinium*, and has now been isolated in the crystalline condition. It forms deep red crystals, m. p. 140° (approx.), which give deep blue solutions in methyl and ethyl alcohols. The solid substance is extremely unstable and it was not found possible to make a determination of its molecular weight.

Halogens react with 1-benzylpyridinium with the formation of 1-benzylpyridinium salts. The salt $(C_{12}H_{12}N)_3[CO(NO_2)_6]$ forms leaflets, m. p. 123° (decomp.).

1 : 1′-Dibenzyltetrahydro-4 : 4′-dipyridyl has the correct molecular

weight in boiling acetone, but shows indications of dissociation in benzene. C. K. I.

Preparation of certain Alkyloxyquinolines and of their Tetrahydro-derivatives. ADOLF SONN and FRITZ BENIRSCHKE (*Ber.*, 1921, **54**, [*B*], 1730—1738).—6-Ethoxyquinoline is most advantageously prepared (yield 53%) by cautiously heating a mixture of *p*-phenetidine, glycerol, concentrated sulphuric acid, and nitrobenzene (hydrochloride [$+2H_2O$], m. p. 224°). It is reduced by tin and concentrated hydrochloric acid to 6-*ethoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, a greenish-yellow liquid, b. p. 164—166°/17 mm., (*hydrochloride*, coarse prisms, m. p. 218°). The latter reacts with potassium cyanate to yield 6-*ethoxytetrahydroquinoline*-1-*carboxylamide*, $OEt\cdot C_9H_9N\cdot CO\cdot NH_2$, colourless, lustrous plates, m. p. 154—155° after previous softening.

6 : 7-*Methylenedioxyquinoline*, pale yellow crystals which gradually become brown when preserved in a vacuum, m. p. 77°, b. p. 180—182°/22 mm. [*hydrochloride*, brown needles, m. p. 273° (decomp.)], is obtained in small yield by the action of glycerol, sulphuric acid, and nitrobenzene on 4-aminocatechol methylene ether (improved methods for the preparation of the latter and of catechol methylene ether are described).

6-Aminopiperonal (the preparation of which is described in detail, cf. Rilliet and Kreitmann, A., 1913, i, 1355) condenses with acetaldehyde in the presence of dilute aqueous alcoholic sodium hydroxide solution to yield a *substance*, probably

$$CH_2O_2{:}C_6H_2(NH_2)\cdot CH(OH)\cdot CH_2\cdot CH{:}N\cdot C_6H_2(CHO){:}O_2CH_2,$$

intensely yellow needles, m. p. 177°.

6 : 7-*Ethylenedioxyquinolines*, coarse crystals, m. p. 97°, b. p. 196°/18 mm. (*hydrochloride*, slender, yellow needles, m. p. 223°), is prepared in 62% yield from 4-aminocatechol ethylene ether, nitrobenzene, sulphuric acid, and glycerol. It is reduced by tin and hydrochloric acid to 6 : 7-*ethylenedioxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, needles, m. p. about 78° (*hydrochloride*, slender, lustrous needles, m. p. 201°), b. p. 207°/20 mm. H. W.

Manufacture of Symmetrical Alkylated *m*-Phenylenediamines. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and ARTHUR BRITTAIN (Brit. Pat. 168689).—Symmetrically alkylated *m*-phenylenediamines are obtained by the action at high temperatures of primary or secondary alkylamines or their salts on resorcinol in aqueous or alcoholic solution, and separation of the alkylated phenylenediamine produced from any unchanged resorcinol and from aminophenolic substances. The presence of sulphurous acid is advantageous to the reaction, and hence the alkylamine sulphites can conveniently be employed. For example, a 67% yield of *m*-phenylenedimethyldiamine is obtained by heating in an autoclave for twelve hours at 125° 55 parts of resorcinol, 66 parts of 35% solution of methylamine sulphite, and 125 parts of 25% aqueous solution of methylamine. The product is separated from unchanged methylamine and resorcinol and from *m*-methylaminophenol by the usual methods, and is finally purified by distillation in a vacuum; it has b. p. 170°/10 mm. G. F. M.

Catalysis. I. Reduction of Uracil to Hydrouracil. TREAT B. JOHNSON and ELMER B. BROWN (*Proc. Nat. Acad. Sci.*, 1921, **7**, 75—77).—The authors have shown that uracil may be quantitatively converted into hydrouracil in the presence of colloidal platinum by gaseous hydrogen. The catalyst is prepared by adding a 10% solution of chloroplatinic acid to a solution of gum arabic and reducing to the metal by gaseous hydrogen. An aqueous solution of uracil is mixed with the catalyst and treated with gaseous hydrogen at a pressure of two atmospheres and at temperature 75—85°. The product is pure hydrouracil, m. p. 272°. J. F. S.

***N*-Alkyl Derivatives and *N*-Carboxylic Esters of Indazole.** K. VON AUWERS and W. SCHAICH (*Ber.*, 1921, **54**, [*B*], 1738—1770; cf. A., 1919, i, 455; 1920, i, 638, 640).—Stereoisomerism has only been observed previously among *N*-acyl derivatives of indazole and not with the alkyl compounds of which the methyl and ethyl derivatives alone have been examined. Since in the former cases the occurrence of the phenomenon appeared to depend, in part, at any rate, on the magnitude of the acyl group, the benzylindazoles have now been examined. In this case, also, stereoisomerism is not observed, but the results are otherwise surprising. The product obtained by the action of benzyl iodide on silver indazole is not identical with the 2-benzylindazole described by Fischer and Blochmann (A., 1902, i, 645), and is identified as 1-benzylindazole. Fischer's compound is obtained by the action of benzyl chloride on indazole at 100°, but in a lengthy series of experiments 1-benzylindazole was prepared uniformly from the same substances at 140—180°, whereas in a second series, carried out under apparently precisely similar conditions, the 2-benzyl derivative was uniformly produced. The reason of this apparent anomaly has not been elucidated, but it is definitely shown that each substance is a primary product and that interconversion does not occur under the experimental conditions adopted.

The unexpected results obtained during the preparation of benzylindazole has led to a re-examination of the alkylation of the parent substance by a considerable number of alkyl haloids. It is found that the two isomerides are produced from indazole and alkyl haloid in the presence of boiling alcoholic alkali hydroxide, the proportions being in general about equal; with allyl bromide the 1-derivative predominates to a marked degree, whilst *iso*propyl bromide gives the 1-isomeride exclusively. Indazole and alkyl haloids at 100° yield the 2-derivatives as sole products, except in the case of *iso*propyl bromide, with which reaction does not take place. Methyl, allyl, and benzyl iodides are the only haloids which react with an ethereal suspension of silver indazole with sufficient rapidity at the ordinary temperature; the former gives exclusively 2-methylindazole under these conditions, thus confirming earlier observations, whereas the two latter yield only the corresponding 1-compounds. With ethyl iodide, it is found that increase in temperature very greatly favours the production of the 1-isomeride, and the same phenomenon is also observed in

a less degree with methyl iodide. The boiling points of the 2-derivatives are uniformly about 25° higher than those of the 1-isomeride, the melting points of the picrates are similarly higher, but the differences exhibited are here irregular.

Indazole-2-carboxylic esters are prepared by boiling indazole with alkyl chloroformates or by the action of the latter on silver indazole at the atmospheric temperature. The methods lead to the production of identical substances in each case, and instances of stereoisomerism as with 2-acetyl-, 2-propionyl-, and 2-benzoyl-indazoles are not observed. The corresponding free acids are exceedingly unstable and readily decompose, even at 0°, into indazole and carbon dioxide. The esters exhibit the remarkable property of eliminating carbon dioxide with greater or less readiness when heated, passing generally into the corresponding alkylindazoles.

The theory of the reactions is discussed at length, and with particular reference to the action of alkyl haloids on silver indazole. The most probable hypothesis appears to be that the two components form initially a loose additive product from which silver haloid is eliminated, leaving for the moment the indazyl and alkyl radicles with free valencies. The former then undergoes isomerisation to an equilibrium mixture in accordance with the scheme $C_6H_4{<}\begin{matrix}CH\\ |\\ N\end{matrix}{>}N- \left[\rightarrow C_6H_4{<}\begin{matrix}CH\\ N\\ |\end{matrix}{>}N-\right] \rightarrow C_6H_4{<}\begin{matrix}CH\\ N\end{matrix}{\geq}N$,

and the subsequent addition of the alkyl group to the 1- or 2-nitrogen atom then depends on the distribution of the free valency in the indazyl radicle and the affinity demand of the alkyl group.

The following individual compounds are described: 1-*Benzylindazole*, colourless, lustrous needles, m. p. 64·5° (*picrate*, coarse, yellow crystals, m. p. 89·5—90·5°). 2-*Benzylindazole*-3-*carboxylic acid*, almost colourless needles, m. p. 194°, which gives 2-benzylindazole, m. p. 67—69° (picrate, m. p. 160—162°) when distilled. 1-*Benzylindazole*-3-*carboxylic acid*, small, colourless needles, m. p. 164·5—165·5°, which when heated is converted into 1-benzylindazole. 1-*Benzyl*-2-*methylindazolium iodide*, $C_6H_4{<}\begin{matrix}CH\\ N(C_7H_7)\end{matrix}{>}N{<}\begin{matrix}Me\\ I\end{matrix}$, needles or coarse prisms, m. p. 175° (corresponding *picrate*, m. p. 139°), which decomposes when heated in a vacuum into a mixture of 2-methylindazole and 1-benzylindazole. 2-*Benzyl*-1-*methylindazolium iodide*, $C_6H_4{<}\begin{matrix}CH\\ NMe\end{matrix}{>}N{<}\begin{matrix}C_7H_7\\ I\end{matrix}$, slender, colourless needles, m. p. 148—149° (corresponding *picrate*, m. p. 195—196°, decomp.), which decomposes into 1-methylindazole when heated in a vacuum (2-benzylindazole when treated with an excess of methyl iodide yields 1 : 2-dimethylindazolium iodide). 1 : 2-*Dimethylindazolium hydroxide*, an almost colourless, crystalline mass which absorbs carbon dioxide readily from the air and yields 1-methylindazole when distilled. 1-*Propylindazole*, a colourless liquid, b. p. 118—119°/10 mm. (*picrate*, yellow needles, m. p. 99—100°). 2-*Propylindazole*, a colourless liquid, b. p. 157°/20 mm. (*picrate*, m. p. 151—152°). 1-iso*Propylindazole*, a colourless liquid, b. p. 117—118°/

12 mm. (*picrate*, yellow needles, m. p. 120°). 1-iso*Amylindazole*, a colourless liquid, b. p. 154—155°/17 mm. [*picrate* (?) m. p. 63—65°]. 2-iso*Amylindazole*, a colourless liquid, b. p. 178—179°/17 mm. (*picrate*, yellow, matted needles, m. p. 115—116°). 1-*Allylindazole*, a colourless liquid, b. p. 126°/12 mm. (*picrate*, slender, yellow needles, m. p. 112·5—113·5°). 2-*Allylindazole*, a colourless liquid, b. p. 144—145°/12 mm. (*picrate*, yellow needles, m. p. 125—126°). *Ethyl indazole-2-carboxylate*, a colourless liquid, b. p. 156°/10 mm. [additive *product* with mercuric chloride, m. p. (indefinite) 115—123°; a picrate is not formed], which decomposes when distilled under diminished pressure into a mixture of 1- and 2-ethylindazoles and is converted by methyl iodide at 100° into 1 : 2-dimethylindazolium iodide. *Methyl indazole-2-carboxylate*, long needles, m. p. 59—60°, b. p. 152—153°/15 mm., which gives much resinous matter and 2-methylindazole when distilled. iso*Amyl indazole-2-carboxylate*, a viscous liquid, b. p. 187·5°/11·5 mm., which, when heated, yields *iso*amyl alcohol, indazole, and 2-*iso*amylindazole. *Benzyl indazole-2-carboxylate*, colourless needles, m. p. 83—84°, which readily yields a mixture of the 1- and 2-benzylindazoles. *Phenyl indazole-2-carboxylate*, colourless, lustrous needles, m. p. 91°, b. p. 215°/11 mm., which yields mainly resinous matter in addition to phenol and indazole when heated at the atmospheric pressure for a considerable time. H. W.

dl-β-2-Furyl-α-alanine. TAKAOKI SASAKI (*Ber.*, 1921, **54**, [*B*], 2056—2059).—The preparation of the substance is effected according to the author's glycine anhydride method (this vol., i, 196).

2 : 5-*Diketo*-3 : 6-*difurfurylidinepiperazine*,

$$C_4H_3O\cdot CH{:}C{<}{\scriptsize\begin{matrix}CO\cdot NH\\NH\cdot CO\end{matrix}}{>}C{:}CH\cdot C_4H_3O,$$

yellow needles, m. p. 289—290° (corr., decomp.), is obtained in 83·7% yield by the action of glycine anhydride on freshly-distilled furfuraldehyde in the presence of acetic anhydride and anhydrous sodium acetate at 120—130°. It is reduced by sodium and alcohol (95%) to 2 : 5-*diketo*-3 : 6-*difurfurylpiperazine*, m. p. 216° (corr.), which is hydrolysed by boiling aqueous barium hydroxide solution to dl-β-2-*furyl-α-alanine*, $C_4H_3O\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, m. p. 260° (corr.); the latter is converted by phenylcarbimide into *α-phenylcarbamido-β-2-furylpropionic acid*,

$$C_4H_3O\cdot CH_2\cdot CH(NH\cdot CO\cdot NHPh)\cdot CO_2H,$$

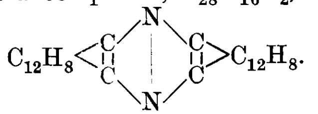
m. p. 162—163° (corr.), and by naphthalene-β-sulphonyl chloride into N-*naphthalenesulphonyl-β-2-furyl-α-alanine*,

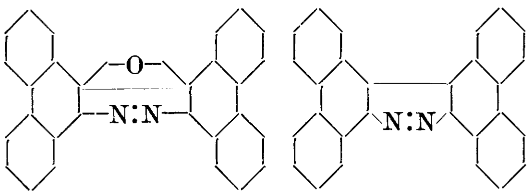
$$C_4H_3O\cdot CH_2\cdot CH(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,$$

decomp. 222° after darkening at 208°. H. W.

o-Chlorodinitrotoluenes. III. Bases derived from 2-Chloro-4 : 5-dinitrotoluene. GILBERT T. MORGAN and WILLIAM ARTHUR PERCIVAL CHALLENOR (T., 1921, **119**, 1537—1546).

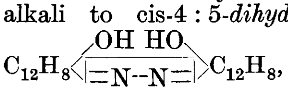
o-Quinones and 1 : 2-Diketones. III. Constitution of Phenanthraquinoneimide Anhydride. A. SCHÖNBERG and BERTA ROSENTHAL (*Ber.*, 1921, **54**, [*B*], 1789—1802).—The elucida-

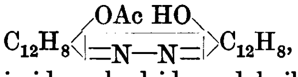
tion of the constitution of acenaphthaquinoneimide anhydride (this vol., i, 275) has induced the authors to investigate phenanthraquinoneimide anhydride. The latter is found to lose its oxygen when heated and to yield a compound, $C_{28}H_{16}N_2$, which is not identical with the azine, . Further, it combines readily in molecular proportions with water, alcohols, acetic acid, and hydrogen chloride, giving products from which the original material is readily regenerated. The latter properties point to the presence of the ethylene oxide ring. The annexed formulæ (I and II) are therefore proposed for the imide anhydride and the corresponding oxygen-free compound.



(I.) (II.)

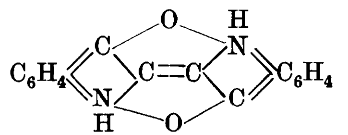
Phenanthraquinoneimide hydrochloride is obtained in the form of extremely unstable, red needles when a dry ethereal solution of hydrogen chloride is slowly added to the imide dissolved in a well-cooled mixture of ether and chloroform. The corresponding *picrate* crystallises in dark red needles, m. p. above 150° (decomp.). Phenanthraquinoneimide anhydride, prepared by short treatment of the imide with boiling acetic anhydride, forms pale yellow needles, m. p. 252° (*picrate*, short, scarlet needles, m. p. 216—217°); it can also be prepared by heating the imide. It is oxidised by chromic acid in glacial acetic acid solution to phenanthraquinone. When heated above 380° it is partly carbonised and gives a sublimate (about 70%) of *diphenanthrapyridazine* (formula II), yellow needles, m. p. 290°, which is converted by chromic acid into phenanthraquinone; it is stable towards boiling alkaline permanganate and is not reduced by zinc dust in acetic acid solution. It yields a *picrolonate* and a *picrate*, yellow needles, m. p. 255—256° after previous softening.

The imide anhydride is readily hydrolysed by solutions of alkali to cis-4 : 5-*dihydroxydiphenanthrapyridazine*-4 : 5-*dihydride*, , colourless prisms (+EtOH), decomp. 305° after loss of alcohol at about 220°, which is readily reconverted into the imide anhydride by treatment with benzoyl chloride according to Schotten-Baumann, by warming with acetic anhydride or by being melted. The action of acids on the imide anhydride results in the utilisation of one molecule for the rupture of the ethylene oxide ring and of a second molecule in the formation of a salt with the basic compound thus formed; the elimination of the second molecule and liberation of the base without affecting the first molecule is a matter of considerable difficulty. The *acetate*,

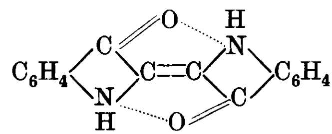
 colourless prisms, is formed from the imide anhydride and boiling glacial acetic acid, and is converted by boiling nitrobenzene into the free *base*, colourless prisms, m. p. 302—305° (violent decomp.); it is hydrolysed in alkaline solution to the corresponding 4 : 5-dihydroxy-compound. cis-4-*Hydroxy*-5-*propionoxydiphenanthrapyridazine*-4 : 5-*dihydride propionate* is prepared in a similar manner, and is converted above 220° into the corresponding free *base*, m. p. 306° (decomp.). The *hydrochloride* of cis-4-*chloro*-5-*hydroxydiphenanthrapyridazine*-4 : 5-*dihydride* is obtained from the imide anhydride and hydrogen chloride in warm chloroform, but the isolation of the corresponding base could not be accomplished satisfactorily. Treatment of the imide anhydride with a boiling solution of sulphuric acid in methyl alcohol leads to the formation of cis-4-*hydroxy*-5-*methoxydiphenanthrapyridazine*-4 : 5-*dihydride*, colourless prisms (+MeOH), m. p. 202°; the corresponding *picrate*, yellow prisms, m. p. 231°, after slight previous softening, and *sulphate*, colourless needles, are described. cis-4-*Hydroxy*-5-*ethoxydiphenanthrapyridazine*-4 : 5-*dihydride* crystallises in colourless prisms, m. p. 180° [the *nitrate*, colourless, rhombic prisms, decomp. 174°, *chloride*, m. p. 227—228° (decomp.) after previous softening, and *picrate*, yellow prisms, m. p. 230°, are described]. cis-4-*Hydroxy*-5-n-*propoxydiphenanthrapyridazine*-4 : 5-*dihydride* forms colourless prisms, m. p. 149°.

H. W.

Indigotin. W. MADELUNG (*Zeitsch. angew. Chem.*, 1921, **34**, 482—483, 486—488).—The question as to how far Baeyer's formula for indigotin is in agreement with the chemical behaviour and physical properties of indigotin, and known facts with regard to the relation between colour and chemical constitution, is critically discussed. It is concluded that the facts are interpreted more correctly by one of the following formulæ:



(I.)

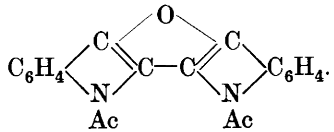


(II.)

The choice between I, which is more nearly related to the conceptions of Claasz, and II, which is more in agreement with the conceptions of Lifschitz and Lourié, is regarded as unimportant, the point of real importance in the proposed formulæ being that the carbonyl and imino-groups are at each end of a five-membered conjugated system, thus O=C—C=C—NH. Such an arrangement is to be found in other vat dyes of both the indigoid and anthracene series, and the stability and technical utility of these dyes are attributed to this atomic grouping, which is as important in this series as is the proximity of the carbonyl and hydroxyl groups in the dyes of the alizarin series, where the chain O=C—C=C—OH plays a

similar rôle. If the above formulæ are accepted, indigotin is to be regarded as a derivative of the coloured and stable modification of dibenzoylethylene.

Indigotin on treatment with acetic anhydride and zinc dust in presence of a little acetyl chloride is converted into diacetylanhydroindigo-white,



The acetyl groups cannot be removed from this compound without far-reaching decomposition. When indigotin in alcoholic hydrochloric acid suspension is reduced with iron powder, a sparingly soluble monohydrochloride of a base is obtained. This base proved to be a hydrogenated anhydroindigo-white containing the hydrofuran ring, and attempts to dehydrogenate this compound with a mild oxidising agent resulted in the formation of anhydroindigo-white, two molecules of whioh then condense, with elimination of water.

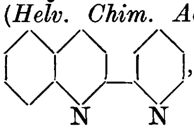
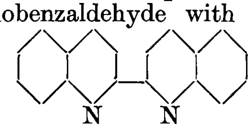
The addition of indigo-white to warm alcoholic hydrochloric acid, with or without the exclusion of air, results in the formation of indigotin and the hydrogenated anhydroindigo-white. F. M. R.

Alkali Fusions. III. Fusion of Phenylglycine-*o*-carboxylic Acid for the Production of Indigotin. MAX PHILLIPS (*J. Ind. Eng. Chem.*, 1921, **13**, 759—762; cf. A., 1920, i, 732).—The maximum yield (89%) of indigotin is obtained when 1 molecule of phenylglycine-*o*-carboxylic acid and 12 to 16 molecules of potassium hydroxide are fused together at 260° for ten minutes. With sodium hydroxide, the maximum yield (69%) is obtained by using 28 to 32 molecules of the alkali and fusing the mixture at 270° for twenty-five to thirty minutes. W. P. S.

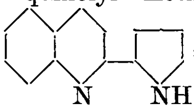
Constitution of the *iso*Isatogens. PAUL RÜGGLI and ADOLF BOLLIGER (*Helv. Chim. Acta*, 1921, **4**, 626—637; cf. A., 1919, i, 221).—The isomerism of the isatogens with the lighter coloured products obtained from them is confirmed by molecular weight determinations of the product derived from methyl isatogenate, and the latter are termed *iso*isatogens. It is suggested that the two series are desmotropic and that the formation of isatin from *o*-nitrophenylpropiolic acid (Baeyer, A., 1886, 274) involves a similar change. The formula previously proposed for the new compounds is not finally adopted, although no evidence has been discovered against it. Thus, the change is not analogous to the change of nitrobenzene into *p*-nitrosophenol, since the *iso*isatogens have no phenolic properties, and methyl *iso*isatogenate is reduced by stannous chloride to methyl indoxylate, although not as readily as methyl isatogenate. Further, the *iso*-esters, either alone or, with less accompanying decomposition, in glacial acetic acid solution are converted by heat into their isomerides. The change is, however, best accomplished by heating the *iso*-compound with phenylcarbimide (cf. Beckmann,

A., 1909, i, 390; Diels and Salomon, A., 1919, i, 226; Staudinger, A., 1919, i, 584). Methyl *iso*isatogenate furnishes an oxime at the ordinary temperature which is identical with that produced from the quinonoid isomeride, and since it exhibits oxidising properties, (cf. Pfeiffer, A., 1916, i, 327) is derived from this. This exceptional observation is unexplained. *Ethyl* iso*isatogenate*, $C_{11}H_9O_4N$, m. p. 146°, forms yellow crystals. *Ethyl* β-o-*nitrophenylbromoacrylate*, $C_{11}H_{10}O_4NBr$, m. p. 59°, results from the action of pyridine on ethyl αβ-dibromo-β-*o*-nitrophenylpropionate. Di-isatogen (Baeyer, A., 1882, 619) is best obtained from *oo*-dinitrodiphenyldiacetylene by illumination of its chloroform solution. J. K.

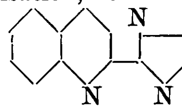
Action of Phenyl Hydrazine on Isatogens. PAUL RÜGGLI and ADOLF BOLLIGER (*Helv. Chim. Acta*, 1921, **4**, 637—644; cf. preceding abstract).—The action of phenylhydrazine on 6-nitro-2-phenylisatogen results in the formation of 6-*nitro*-2-*phenylindoxyl*, $C_{14}H_{10}O_3N_2$, orange-red leaflets, m. p. 215.° Its dilute solution in acetic anhydride in presence of sulphuric acid furnishes an α-*acetyl* derivative, $C_{16}H_{12}O_4N_2$, orange-yellow needles, m. p. 192—193°, whilst in more concentrated solution at 40° an isomeric β-*derivative*, $C_{16}H_{12}O_4N_2$, greenish-yellow needles, m. p. 172°, is produced. 6-Nitro-2-phenylindoxyl yields a *quinhydrone*, $C_{28}H_{18}O_7N_4$, brownish-black needles, m. p. 208—210°, when mixed in hot glacial acetic acid solution with 6-nitro-2-phenylisatogen, but not with its isomeride. The latter is also distinguished by its conversion by means of phenylhydrazine into 6-*nitro*-3-*keto*-2-*phenylindoleninephenylhydrazone*, $C_{20}H_{14}O_2N_4$, red needles, m. p. 260—261°. *Methyl* 3-*ketoindolenine*-2-*carboxylate*, $C_{10}H_7O_3N$, yellow needles, m. p. 255° (decomp.), (*oxime*, $C_{10}H_8O_3N_2$, yellow needles, m. p. 221°) is obtained by the action of phenylhydrazine on a cold dilute solution of methyl isatogenate, but at higher temperatures methyl indoxylate is produced, accompanied by what is probably *methyl* 3-*ketoindolenine*-2-*carboxylate-phenylhydrazone*, $C_{16}H_{13}O_2N_3$, orange crystals, m. p. 218°, when the reaction is particularly energetic. Methyl *iso*isatogenate does not react with phenylhydrazine. J. K.

Paired Cyclamines. I. 2-(2-Quinolyl)Cyclamines; Valency Formula of Quinoline. ALEXANDER P. SMIRNOV (*Helv. Chim. Acta*, 1921, **4**, 802—811).—2-(2'-*Pyridyl*)*quinoline*, , m. p. 99° (*platinichloride*, orange-yellow needles, m. p. 197°, decomp.; *aurichloride*, yellow needles, m. p. 211°, decomp.; *picrate*, greenish-yellow leaflets, m. p. 183°), results from the condensation of *o*-aminobenzaldehyde with 2-pyridyl methyl ketone. 2 : 2'-*Diquinolyl*, , leaflets, m. p. 196° (*platinichloride*, orange-yellow leaflets, m. p. above 300°;

aurichloride, unstable yellow needles; *picrate*, yellow needles, m. p. 210°), formed by condensation of *o*-aminobenzaldehyde with either 2-quinolyl methyl ketone or diacetyl. 2-(2′-*Pyrryl*)*quinoline*,

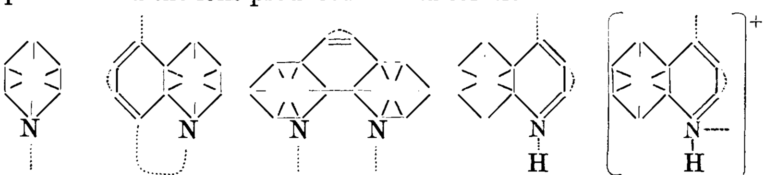


, leaflets, m. p. 129° (*platinichloride*, yellowish-brown prisms, m. p. 210°, decomp.; *aurichloride*, yellow and unstable), prepared similarly from *o*-aminobenzaldehyde or from potassium pyrrole and 2-chloroquinoline followed by isomerisation, colours a pine-shaving yellow. 2-(2′-*Glyoxalinyl*)*quinoline*,



, prisms, m. p. 119° [*platinichloride*, orange prisms, m. p. 330° (decomp.); *aurichloride*, golden-yellow leaflets, m. p. 205° (decomp.); *picrate*, needles, m. p. 201°], prepared from the silver salt of glyoxaline and 2-chloroquinoline.

2-(2′-Pyridyl)- and 2-(2′-quinolyl)-quinolines do not form complex ferro-compounds as do 2 : 2′-dipyridyl and *o*-phenanthroline (Blau, A., 1899, i, 387). This is attributed to internal saturation of the residual nitrogen valency in the former compounds, the differences being expressed by the formulæ (I—III), which also explain the destruction of the " benzene " nucleus by alkaline oxidation. The attack of the pyridine ring by reduction or acid oxidation is explained by assuming formulæ IV and V for the primary reduction product and the ions produced in acid solution.



(I.) (II.) (III.) (IV.) (V.)

J. K.

Ring Closure with Hydrazinedicarbonamides containing Sulphur. I. Dithiourazole and Iminothiourazole. F. Arndt and E. Milde (*Ber.*, 1921, **54**, [*B*], 2089—2110).—The products of the internal condensation of hydrazinedithiocarbonamide and hydrazinedicarbothiophenylamide have been examined by Freund (A., 1894, i, 97; 1895, i, 400), who considered them to be derivatives of thiourazole, and later by Busch and Schmidt (A., 1913, i, 907) and by Busch and Lotz (A., 1915, i, 317), who proved them to be thiodiazoles. The internal condensation of the methyl and benzyl ethers of hydrazinedithiocarbonamide has now been investigated.

Hydrazinedithiocarbonamide is readily methylated by methyl sulphate in aqueous alkaline solution and the production of the mono- or di-methylated product is easily regulated by suitably adjusting the quantity of sodium hydroxide used. *Hydrazinedithiocarbonamide monomethyl ether*, $NH_2\cdot CS\cdot NH\cdot NH\cdot C(SMe){:}NH$, crys-

tallises in lustrous needles, m. p. 174°, whereas the *dimethyl* compound, $N_2H_2[C(SMe)\colon NH]_2$, forms broad needles, m. p. 132°; the *nitrate* and *sulphate* of the latter are freely soluble in water; the *dihydrochloride* has m. p. 198°. The dimethyl compound loses methyl mercaptan at 155—200° and forms *iminomethylthiolurazole*, $NH<\begin{matrix}C(\colon NH)\cdot NH\\ C(SMe)\colon N\end{matrix}$, colourless crystals, m. p. 135°, which is also formed when the compound is boiled with 2*N*-sodium hydroxide solution or when an alcoholic solution of dimethyl cyanimidodithiocarbonate, $C(SMe)_2\colon N\cdot C\colon N$, is boiled with hydrazine hydrate the corresponding *nitrate*, m. p. 157°, *mono-silver* salt and *monobenzoate*, m. p. 144—145°, are described.

Iminothiourazole, $NH<\begin{matrix}C(\colon NH)\cdot NH\\ CS\text{———}NH\end{matrix}$, short, colourless needles, m. p. 303° (decomp.), is prepared by the action of very concentrated, aqueous potassium hydroxide solution on hydrazinedithiocarbonamide, of 2*N*-sodium hydroxide solution on hydrazinedithiocarbonamide monomethyl ether or of hydrazine hydrate on thiocyanic acid. It is a powerful acid and does not exhibit any basic characteristics. Its constitution is elucidated by its conversion into iminothiourazole monomethyl ether by methyl sulphate and sodium hydroxide. With ammoniacal silver nitrate it gives a *di-silver* salt, whereas in dilute nitric acid solution a *mono-silver* compound is produced. The (?) *dibenzoyl* derivative, lustrous needles, m. p. 177°, is described. Its solution in aqueous sodium hydroxide is oxidised by potassium ferricyanide to the corresponding *disulphide*, colourless crystals, m. p. 240° (decomp.), after softening at 238° [*nitrate*, m. p. 130° (violent decomp.)]. 2 : 5-*Dimethylthiolurazole*, $NH<\begin{matrix}C(SMe)\colon N\\ C(SMe)\colon N\end{matrix}$, colourless needles, m. p. 91° after softening at 90°, is prepared by the action of boiling aqueous 2*N*-sulphuric acid on hydrazinedithiocarbonamide dimethyl ether; the *nitrate*, long, slender needles, m. p. 95°, *silver* salt and *monobenzoate*, m. p. 95°, are described. When treated with fuming hydriodic acid it gives *methylthiolthiourazole*, almost colourless needles, m. p. 254° (decomp.) after softening at 250° (complete demethylation does not appear to occur), the constitution of which is elucidated by its ready re-conversion into the initial substance under the action of methyl sulphate and alkali hydroxide. The monomethyl compound is oxidised by potassium ferricyanide to the corresponding *disulphide*, $C_6H_8N_6S_4$, m. p. 203° after softening at 201°, the *nitrate* of which was also prepared.

Dithiourazole, $NH<\begin{matrix}CS\cdot NH\\ CS\cdot NH\end{matrix}$, almost colourless crystals, m. p. 195—196°, is obtained under certain conditions which are described fully in the original by the action of hydrazine hydrate on methyl trithioallophanate, $SMe\cdot CS\cdot NH\cdot CS\cdot NH_2$, in aqueous solution; the *silver* salts, $C_2HN_3S_2Ag_2$ and $C_2N_3S_2Ag_3$, are prepared in dilute acid and ammoniacal solutions respectively.

Hydrazinedithiocarbonamide monomethyl ether is transformed by

boiling $2N$-hydrochloric acid into *methylthioliminothiodiazole*, $S<\begin{matrix}C(:NH)\cdot NH \\ C(SMe):N\end{matrix}$, long pointed needles, m. p. 176—178° (the sparingly soluble *hydrochloride* and the *silver* salt are described); the constitution of the substance is deduced from its markedly basic properties, from its production by the methylation of the thioliminothiodiazole of Freund (*loc. cit.*) and Busch (*loc. cit.*), and by the direct synthesis of the compound of the only alternative formula, $NH<\begin{matrix}C(SH)=N \\ C(SMe):N\end{matrix}$, which has completely different properties.

Hydrazinedithiocarbonamide is converted by benzyl chloride in the presence of aqueous potassium hydroxide solution into the corresponding *monobenzyl ether*, short, coarse needles, m. p. 148° [which is transformed by sulphuric acid into benzylthioliminothiodiazole, m. p. 157° (cf. Busch, *loc. cit.*) and by sodium hydroxide into benzyl mercaptan and iminothiourazole] and the *dibenzyl ether*, lustrous leaflets, m. p. 94° (which readily yields sparingly soluble *salts* with mineral acids and is remarkably resistant towards the action of heat and of alkali). The latter is converted by $2N$-sulphuric acid in aqueous alcoholic solution into 2 : 5-*dibenzylthiolurazole*, m. p. 111° after softening at 108°.

Hydrazinedithiocarbophenylamide is transformed by boiling $2N$-sodium hydroxide solution into 2-phenylimino-5-thio-1-phenylurazole, m. p. 205° (cf. Busch, *loc. cit.*). It is transformed by methyl sulphate into the corresponding *dimethyl* derivative, $C_{16}H_{18}N_4S_2$, lustrous needles, m. p. 140°. The latter is converted by acids or by potassium hydroxide solution into methyl mercaptan and phenylmethylthiolphenylurazole, m. p. 226°. H. W.

5-Hydroxyhydantoin. HEINRICH BILTZ and MARIA KOBEL (*Ber.*, 1921, **54**, [*B*], 1802—1828).—Several substances are described in the literature as glyoxylurea [5-hydroxyhydantoin]; of these, Strecker's and Medicus's (this Journ., 1875, 555) " crystalline glyoxylurea " has recently been shown to be identical with allantoxaidin (Biltz and Robl, A., 1920, i, 885). The authors now investigate the amorphous products.

In the preliminary part of the work, attempts to isolate glyoxylurea from uroxanic acid, from allantoin, and from allanturic acid according to directions given in the literature are described. It appears to be impossible, however, to isolate a pure glyoxylurea, $C_3H_4O_3N_2$, from these materials, the main difficulty consisting in the removal of allantoin; even when this has been largely eliminated, a pure product is not obtained and the only possibilities of success appear to lie in the selection of an original material which cannot yield allantoin or in the choice of conditions under which the latter is destroyed. The latter effect can be achieved by treatment of the crude product with nitrous fumes, or preferably successively with hot hydrochloric acid and nitrous fumes; the purified product then gives analytical data approximating to those required by the formula $C_3H_4O_3N_2$. As starting-point for the experiments in the former direction, alloxanic acid [5-hydroxy-

hydantoin-5-carboxylic acid] (Biltz, Heyn, and Bergius, A., 1917, i, 289) is chosen. An improved method of preparing this substance from alloxan is fully described, and it is shown to be decomposed by hot water into Schlieper's leucoturic acid, a second substance (see later), and difluan, $C_3H_4O_3N_2$, a white, amorphous, voluminous powder which is extremely hygroscopic; it suffers incipient decomposition at 120° and becomes brown at 180°. It is thus possible in two ways to secure preparations, $C_3H_4O_3N_2$, which are precisely similar in all their properties and constitute the main component of the " amorphous glyoxylurea " of the literature. The substance is stable towards hydrochloric acid, but is converted by concentrated sulphuric acid into oxalic acid and ammonia. It is strongly acidic, and liberates carbon dioxide from sodium carbonate. It is very sensitive to the action of alkali hydroxides, yielding oxalic acid, and carbamide or ammonia. This property renders the preparation of well-defined salts a matter of considerable difficulty, but a revision of the recorded data appears to indicate strongly that the material is a monobasic acid. It is smoothly, but under somewhat energetic conditions, oxidised by potassium dichromate and sulphuric acid to parabanic acid. It cannot be reduced by phosphorus and fuming hydriodic acid to hydantoin. Its failure to react with phenylcarbimide indicates the absence of a hydroxyl group. Since, further, the physical and chemical properties differ widely from those of 5-hydroxy-1 : 3-dimethylhydantoin (succeeding abstract), the authors are drawn to the conclusion that their product is not 5-hydroxyhydantoin, but dehydrohydantoic acid, $NH_2\cdot CO\cdot N:CH\cdot CO_2H$. (It is proposed to retain the name " glyoxylurea.") This conception is confirmed by its transformation with diazomethane into *methyl* N-*methyldehydrohydantoate*,

$$NHMe\cdot CO\cdot N:CH\cdot CO_2Me,$$

an amorphous, extremely hygroscopic powder, with benzoic anhydride into the corresponding mixed *anhydride*, $C_{10}H_8O_4N_2$, forming pale yellow, micro-crystalline needles, m. p. 252° (decomp.) after darkening at 220°, and with acetic anhydride into a *substance*, $C_5H_6O_4N_2$, an almost colourless, very hygroscopic powder. It is attacked only with difficulty by nitrous acid.

The authors' hypothesis receives considerable confirmation from the isolation of 5-hydroxyhydantoin which, although previously nearly completely overlooked, is now shown to be the main product of the decomposition of alloxanic acid by water,

$$CO<\begin{matrix}NH\cdot C(OH)\cdot CO_2H\\NH\cdot CO\end{matrix} \longrightarrow CO_2+CO<\begin{matrix}NH\cdot CH\cdot OH\\NH\cdot CO\end{matrix}.$$

The main portion is mixed with the leucoturic acid, from which it is readily separable by taking advantage of its ready solubility in alcohol, in which the latter is insoluble. 5-Hydroxyhydantoin crystallises in needles, m. p. 165°. It is very stable towards alkali, faintly acid towards litmus, and does not liberate carbon dioxide from metallic carbonates. It is oxidised by potassium dichromate to parabanic acid, and reduced by hydriodic acid to hydantoin. It is readily converted by diazomethane into 5-*methoxy*-3-*methylhydantoin*, a yellow, extremely hygroscopic syrup which is trans-

formed by hydriodic acid into methyl iodide and 3-methylhydantoin, m. p. 184—185°. The *barium* salt, $C_3H_2O_3N_2Ba$, is described. It is converted by prolonged treatment with hot water into glyoxylurea.

Leucoturic acid has been further examined and is definitely proved to be identical with oxalantin isolated by Limpricht by the reduction of parabanic acid with zinc and dilute acid. (Since the substance is shown to be a monobasic acid, the retention of the name "leucoturic acid" is proposed.) The original formula, $C_6H_6O_6N_4$, is confirmed. The substance forms ill-defined crystals, m. p. 238°. It is acid towards litmus, and liberates carbon dioxide from metallic carbonates. It is converted by solutions of alkali hydroxides into oxalic acid and ammonia, and by concentrated aqueous ammonia into ammonium oxalurate and dehydrohydantoate. It is oxidised by potassium dichromate to parabanic acid, but does not yield hydantoin under the action of hydriodic acid and phosphonium iodide. It is converted by diazomethane into *methyl dimethylleucoturate*, ill-defined leaflets, m. p. 230° (decomp.), in which one methyl group is shown to be attached to oxygen and the other two groups to nitrogen. The constitution of the compound is in all probability expressed by the formula

$$NH_2{\cdot}CO{\cdot}N{:}CH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2H;$$

attempts to synthetise it from oxaluric acid and glyoxylurea were not successful. H. W.

5-Hydroxy-1 : 3-dimethylhydantoin. HEINRICH BILTZ and DOROTHEA HEIDRICH (*Ber.*, 1921, **54**, [*B*], 1829—1833).—The substance has been prepared previously by Andreasch (A., 1882, 1054) by the reduction of 1 : 3-dimethylparabanic acid, and its constitution has been established. The present investigation was undertaken with the object of supplying further information required in the investigation of glyoxylurea (preceding abstract).

Full details of an improved method for the isolation of dimethylparabanic acid from caffeine are recorded and also for the crystallisation of 5-hydroxy-1 : 3-dimethylhydantoin; the latter has m. p. 70° after softening at 65°, b. p. about 283—284°. It is reduced by concentrated hydriodic acid to 1 : 3-dimethylhydantoin, m. p. 45—46°. It is converted by benzoic anhydride into the corresponding *benzoate*, small prisms, m. p. 122—123°, by phenylcarbimide into the *phenylcarbamate*, m. p. 147—148° after softening at 145°, and by diazomethane into 5-*methoxy*-1 : 3-*dimethylhydantoin*, which could only be obtained on one occasion in the crystalline form. It is oxidised by potassium dichromate to 1 : 3-dimethylparabanic acid. H. W.

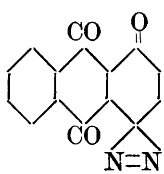
Non-aromatic Diazonium Salts. VII. The Diazo-reaction in the *iso*Oxazole Series. GILBERT T. MORGAN and HENRY BURGESS (T., 1921, **119**, 1546—1549).

Azides, Anthranils, and Azo-derivatives of Anthraquinone. LUDWIG GATTERMANN and HANS ROLFES (*Annalen*, 1921, **425**, 135—161).—Anthraquinone-2-diazonium sulphate, on treatment

with hydrazine sulphate, yields 2-azidoanthraquinone, which shows no tendency to pass into an isomeride of 3 : 4-benzoyleneanthranil (Schaarschmidt, A., 1916, i, 856), a fact favouring Schaarschmidt's formula for the anthranil as against the "semiazo" formula of Gattermann and Ebert (A., 1916, i, 857). 2-Azidoanthraquinone, on condensation with ethyl acetoacetate, yields *ethyl* 1-β-*anthraquinonyl*-5-*methyltriazole*-4-*carboxylate*, m. p. 201° (decomp.).

3 : 4-Benzoyleneanthranil may be obtained by treating anthraquinone-1-diazonium sulphate with hydrazine sulphate, and 5-*nitro*-3 : 4-*benzoyleneanthranil* by nitrating 1-azidoanthraquinone by means of fuming nitric acid in the cold. 5-Nitro-3 : 4-benzoyleneanthranil forms brown needles, m. p. 244—245°, gives with concentrated sulphuric acid a solution which on heating at 170° with boric acid becomes deep red and strongly fluorescent, and gives 1 : 4-diaminoanthraquinone on reduction by sodium sulphide. It may also be prepared by the following series of reactions. 1-Nitro-4-aminoanthraquinone, when treated with nitrous acid and a salt of hydroxylamine, yields 4-*nitro*-1-*anthraquinoneazohydroxylamide*, $C_{14}H_7O_2N_2{\cdot}NH{\cdot}OH$, unstable, red rhombs, which on heating with pyridine and acetic anhydride yields 4-*nitro*-1-*azidoanthraquinone*. This substance, which forms yellow needles, on heating either alone or in benzene eliminates nitrogen and yields the nitrobenzoyleneanthranil.

A solution of 4-nitro-1-anthraquinonediazonium sulphate on keeping gradually deposits red needles, termed by the authors "1 : 4-*anthraquinonequinonediazide*" (formula annexed). On heating this with concentrated sulphuric acid, quinizarine is produced.



4-*Chloro*-1-*anthraquinoneazohydroxylamide* is prepared from 4-chloro-1-aminoanthraquinone. It crystallises from pyridine with 1 mol. of this substance, and passes into 4-*chloro*-1-*azidoanthraquinone* on treatment with pyridine and acetic anhydride, or with pyridine formaldehyde and dilute aqueous sodium hydroxide. 4-Chloro-1-azidoanthraquinone on nitration yields 5-*chloro*-7-*nitro*-3 : 4-*benzoyleneanthranil*, yellow needles, which decompose at 187°.

1-*Anthraquinoneazohydroxylamide*-5-*diazonium sulphate*, bronze needles, is prepared from 1 : 5-diaminoanthraquinone, and on treatment with pyridine yields 1-N-*pyridyl*-5-*anthraquinoneazohydroxylamide*, red, lancet-like crystals, which with pyridine and acetic anhydride yields 3 : 4-*o*-N-*pyridylbenzoyleneanthranil*, golden-yellow, glistening leaflets, m. p. above 300°.

The following azo-compounds are described: p-1-*Anthraquinoneazodimethylaniline*, dark brown prisms, m. p. 249°. p-1-*Anthraquinoneazoaniline*, red needles, m. p. 211° (decomp.). m-1-*Anthraquinoneazo*-p-*toluidine*, deep red needles, m. p. 230°. p-1-*Anthraquinoneazophenol*, fiery red tablets. p-1-*Anthraquinoneazoresorcinol* crystallises from aniline in red needles having 1 mol. of aniline. p-1 : 5-*Aminoanthraquinoneazoaniline*, red needles, m. p. 216°. p-1 : 5-*Anthraquinoneazohydroxylamideazodimethylaniline*, dark red

tablets containing 1 mol. of pyridine. (With pyridine and acetic anhydride it yields o-3 : 4-p-*dimethylanilineazobenzoyleneanthranil*, glistening, dark brown rhombs, m. p. 229°.) 1 : 1-*Anthraquinoneazo-β-naphthol*, fiery red needles, m. p. 290°. pp-1 : 5-*Anthraquinonebisazoaniline*, red rhombs, decomposing at 251°. mm-1 : 5-*Anthraquinonebisazo*-p-*toluidine*, dark red needles, m. p. 246° (decomp.). p-2-*Anthraquinoneazodimethylaniline*, needles having indefinite m. p. p-2-*Anthraquinoneazoaniline*, yellow needles. m-2-*Anthraquinoneazo*-p-*toluidine*, red rhombs, m. p. 227° (decomp.). p-2-*Anthraquinoneazophenol*, bright red needles. 2-*Anthraquinoneazo-β-naphthol*, red needles, m. p. 250°. 4 : 2-*Anthraquinoneazo-α-naphthylamine*, needles, m. p. above 290°. *Ethyl* α-1-*anthraquinoneazoacetoacetate*, orange-yellow needles, m. p. 152° (*phenylhydrazone*, red needles, m. p. 263°). *Ethyl* α-2-*anthraquinoneazoacetoacetate*, small, yellow needles, m. p. 221° (*phenylhydrazone*, red rhombs, m. p. 247°). All these substances are prepared by coupling the anthraquinonediazonium salts with appropriate second components.

α-1-*Anthraquinoneazoacetoacetic acid*, yellow needles, m. p. 251°, is prepared by hydrolysis of the ester. On condensing with phenylhydrazine, it yields 4 : 1-*anthraquinoneazo*-1-*phenyl*-3-*methylpyrazolone*, red needles, m. p. 252°. α-2-*Anthraquinoneazoacetoacetic acid*, small, yellow tablets, m. p. 247°, and 4 : 2-*anthraquinone*-1-*phenyl*-3-*methylpyrazolone*, bronze leaflets, m. p. 268°, are prepared in a similar manner. C. K. I.

The Proteins and Colloid Chemistry. JACQUES LOEB (*Science*, 1920, **52**, 449—456).—An address in which evidence is put forward that, as exhibited by the behaviour of the proteins, the chemistry of colloids does not differ from the chemistry of crystalloids. It can be shown that ions combine with protein in the typical ratio in which the same ions combine with crystalloids only when it is recognised that the hydrogen-ion concentration of the protein solution determines the amount of ion combined with the protein, and the true comparison of one ion with another can only be made at the same hydrogen-ion concentration. The results of Hofmeister and of Pauli are invalid owing to non-observance of this condition. Only the kation or the anion, or neither, can combine with protein, according to the hydrogen-ion concentration of the solution. For example, gelatin at the isoelectric point, $p_H=4\cdot7$, combines with neither ion; at $p_H > 4\cdot7$ only with kations (sodium gelatinate), at $p_H < 4\cdot7$ only with anions (gelatin chloride). This can be shown when powdered gelatin, brought to various values for p_H, is treated on a filter with a neutral salt (for example, silver nitrate, nickel chloride, potassium ferrocyanide, and sodium thiocyanate) solution and the excess of salt washed away. It follows that values for both concentration and hydrogen-ion concentration are necessary to define a protein solution.

When acid is added to isoelectric gelatin (or other protein), equilibrium is established between acid, gelatin–acid salt, and isoelectric gelatin; when alkali is added, equilibrium is established between metal gelatinate, isoelectric protein, and hydrogen ions.

That the nature of the union is chemical is shown by the fact that three volumes of $0{\cdot}1N$-phosphoric acid, or two volumes of $0{\cdot}1N$-oxalic acid, or one volume of $0{\cdot}1N$-hydrochloric, nitric, or sulphuric acid are required to bring a quantity of 1% gelatin solution to the same hydrogen-ion concentration. When this hydrogen-ion concentration is reached, the gelatin is in each case in combination with the same amount of acid, and the solutions show the same osmotic pressure. Analogous results are shown with bases, and with both bases and acids in the case of egg-albumin.

From these combining ratios the physical properties of proteins can be predicted. Any acid of which the anion behaves as a univalent ion raises the osmotic pressure, viscosity, and swelling of protein approximately twice as much as one of which the anion behaves as a bivalent ion; kations conform to the same rule. Curves in which the hydrogen-ion concentrations are plotted against the magnitude of certain physical properties (for example, swelling) indicate almost identical effects with chloride, bromide, nitrate, tartrate, succinate, citrate, and phosphate, with a minimum at $p_H = 4{\cdot}7$ and a maximum at about $p_H = 3{\cdot}2$; gelatin sulphate gives parallel curves, but the maximum value is only half that obtained previously. Protein salts with ions of the same valency show at the same hydrogen-ion concentrations like physical properties. CHEMICAL ABSTRACTS.

Colorimetric Experiments on Tryptophan. IV. Formation of Melanoidin by the Acid Hydrolysis of Protein and its Dependance on Tryptophan Complexes. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Zeitsch.*, 1921, **116**, 224—231).—By investigating the tryptophan content of various proteins colorimetrically and determining the amount of melanoidin formed on acid hydrolysis, a parallelism is observed between the tryptophan content and the melanoidin. The authors consider that the melanoidins are the condensation products of the tryptophan molecules. The term humin is reserved for the results of change of carbohydrate complexes. H. K.

Relation between the Salting-out and Precipitation-inhibiting action of Inorganic Ions on Protein Solutions. RICHARD LABES (*Pflüger's Archiv*, 1921, **186**, 112—125).—Inorganic ions influence the precipitation optimum of serum-albumin. With increasing concentrations of a neutral alkali salt the precipitation is displaced more and more into the region of higher acidity, up to the zone of the salting-out optimum. The neutral salts in extreme acid reactions salt out the best and the displacement of the precipitation optimum by the more strongly absorbed anions of the neutral alkali salts is to be found on the acid side.

CHEMICAL ABSTRACTS.

Displacement of the Precipitation Optimum of Serum-albumin by Alkaloids, Dyes, and other Organic Electrolytes, and the Action of Non-electrolytes. RICHARD LABES (*Pflüger's Archiv*, 1921, **186**, 98—111).—The effect of various substances

on the precipitation of serum-albumin is twofold: (1) a displacement of the precipitation optimum, and (2) an inhibition or activation of the precipitation. These actions are exerted by organic salts in the form of chlorides just as by inorganic salts. Displacement toward the less acid side increases with the kations in the series: choline, physostigmine, morphine, pilocarpine, cocaine, quinine, optochin, and eucupinotoxin. Displacement toward the acid side increases with the anions in the series: resorcinol, phenol, thymol, naphthol, salicylic acid, eosin, diamine-red. All the anions investigated increase the precipitation more or less; inhibiting anions, as the sulphate ion, are not found among the organic anions. Non-electrolytes (ethyl, methyl, and heptyl alcohols; ethyl ether) never cause a displacement but only a broadening of the precipitation zone. Their effect is in striking parallel with their surface activity. CHEMICAL ABSTRACTS.

Acerin: the Globulin of the Maple Seed. R. J. ANDERSON [with W. L. KULP] (*J. Biol. Chem.*, 1921, **48**, 23—32).—The globulin of the maple seed, isolated and purified by various methods, is found to be a non-crystalline substance of the elementary composition: C, 51·44%; H, 6·80%; N, 18·34%; O, 22·87%; S, 0·55%. It closely resembles arachin (A., 1917, i, 191), the globulin of the peanut, in its composition and distribution of basic nitrogen; the figures for the latter for acerin are: Cystine, 0·55%; histidine, 1·43%; arginine, 10·07%; lysine, 6·07%. C. R. H.

Physico-chemical Examination of Hæmoglobin. State of Aggregation of Hæmoglobin Molecules. M. CAMIS (*Folia Hæmatologica* 2, 149—211; from *Chem. Zentr.*, 1921, iii, 418).—The surface tension of dialysed hæmoglobin solutions, measured stalagmometrically, decreases with rise of temperature and increases with increase of concentration up to 6%. Addition of 0·006—0·1% of lactic acid to a solution of hæmoglobin or laked blood diminishes surface tension and lowers the extinction coefficient. Both effects are attributable to a decrease in the number of particles. It is supposed that the presence of lactic acid in blood leads to an aggregation of hæmoglobin molecules. G. W. R.

Preparation and Analysis of Animal Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1921, **48**, 177—183).—Improved methods for the preparation of nucleic acids from the spleen, pancreas, and liver are described and analytical results given. For purposes of estimation, the purine bases are separated in the form of their hydrochlorides by alcoholysis of the nucleic acid. No confirmation was obtained of the presence of mixed nucleic acids, that is, nucleic acids containing both hexose and pentose nucleotides (cf. Feulgen, this vol., i, 76). E. S.

The Structure of Thymus-Nucleic Acid and its Possible Bearing on the Structure of Plant-Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1921, **48**, 119—125).—The author's ester formula (A., 1920, i, 193) still expresses all the known facts about the structure of yeast-nucleic acid. Jones's experiments (A., 1920, i,

687) on the rate of hydrolysis of yeast–nucleic acid are in agreement with this formula, and not with the ether theory of union by carbohydrates; they merely indicate that the union between the four nucleotides is more labile than that between the phosphoric acid and carbohydrate. The fact that there is no change in acidity during its hydrolysis by pig pancreas (Jones, A., 1920, i, 687) is due mainly to buffer effect.

From the hydrolysis product of thymus–nucleic acid, hexathymidine diphosphoric acid and hexacytidinediphosphoric acid were isolated by a simplified process and the barium salt of the former was obtained in a crystalline condition. Under the experimental conditions neither the monophosphoric nucleotides nor the dinucleotide previously obtained (Levene and Jacobs, A., 1912, i, 926) could be isolated. The former are therefore probably secondary products, while the existence of the latter is doubtful. In these circumstances, and by analogy with yeast–nucleic acid, the following structure for thymus–nucleic acid is suggested:

$$\begin{array}{ccccccccccccc} & & O & & & & O & & & & O & & \\ & & \| & & & & \| & & & & \| & & \\ C_6H_{10}O_4 & -O- & P & -O- & C_6H_9O_3 & -O- & P & -O- & C_6H_9O_3 & -O- & P & -O- & C_6H_{10}O_4 \\ | & & | & & | & & | & & | & & | & & | \\ C_5H_4N_5 & & OH & & C_5H_5O_2N_2 & & OH & & C_5H_4ON_5 & & OH & & C_4H_4ON_3. \end{array}$$

E. S.

Donnan Equilibrium and the Physical Properties of Proteins. IV. Viscosity (*cont.*). JACQUES LOEB (*J. gen. Physiol.*, 1921, **4**, 73—95; cf. this vol., i, 693).—After completing the proof that the viscosity of suspensions of powdered gelatin in water is influenced by electrolytes in the same way as the viscosity of solutions of gelatin, viscosity measurements are given to show that solutions of gelatin contain (submicroscopic) particles of solid jelly capable of swelling, and that the viscosity is due to those. The viscosity of a solution of isoelectric albumin (which exists in isolated molecules) changes linearly with the concentration, whilst gelatin, especially at low temperature, behaves in a radically different manner. Experiments on the viscosity and sedimentation of suspensions and solutions of casein chloride show that particles of casein chloride occlude water in accordance with a Donnan equilibrium between them and the surrounding liquid. In a colloid solution in general there may be isolated ions and molecules, giving rise to a general viscosity of low order, and also (submicroscopic) particles, the volume of which changes in accordance with the Donnan equilibrium, causing a high viscosity which is markedly influenced by the P_H of the solution and by the dissolved electrolytes.

W. O. K.

The Reciprocal Relation between the Osmotic Pressure and the Viscosity of Gelatin Solutions. JACQUES LOEB (*J. gen. Physiol.*, 1921, **4**, 97—112; cf. preceding abstract).—The osmotic pressure of a gelatin suspension is due almost entirely to the presence of free molecules of the gelatin, the viscosity to the submicroscopic particles swollen in accordance with the Donnan

equilibrium. Thus in a solution of given concentration the larger the osmotic pressure the smaller the viscosity and vice versa. Experiments are described which verify this conclusion.

W. O. K.

Comparative Hydrolysis of Gelatin by Pepsin, Trypsin, Acid, and Alkali. JOHN H. NORTHROP (*J. gen. Physiol.*, 1921, **4**, 57—71).—The relative power of various hydrolysing agents to split protein linkings can be investigated by the following method. Gelatin partly hydrolysed by one agent is submitted to another, and hydrolysis, as indicated by "formal" titration, proceeds further than with either separately if they hydrolyse different linkings. On considerations such as this, it is found that linkings split by trypsin or pepsin are resistant to acid and easily hydrolysed by alkali; those split by pepsin are split by trypsin, although not necessarily vice versa; and of those split by both, rapid pepsin hydrolysis is associated with slow trypsin hydrolysis. W. O. K.

Invertase. RICHARD WILLSTÄTTER and FRITZ RACKE (*Annalen*, 1921, **425**, 1—135).—An examination of the conditions controlling the extraction of invertase from yeast is followed by a study of the adsorption of invertase from the yeast extract on kaolin, aluminium hydroxide and other substances, and the knowledge thus gained is applied to the preparation of invertase having a higher degree of purity than any yet obtained.

The extraction of invertase from yeast by digesting with water is by no means a purely physical process, some decomposition (autolysis), probably enzymatic, being necessary to bring about liberation of the invertase. For instance, the destruction of the yeast-cells by grinding with sand, although it facilitates the subsequent extraction, does not render the invertase immediately soluble.

The yield of invertase from a given specimen of yeast depends greatly on the past history of the latter; if it be dry yeast, the manner of drying is important. For instance, yeast dried at 100°, or by treating with acetone, gives poor yields of invertase. The chief factors which influence the speed of autolysis are dilution with water and the addition of antiseptics (for example, toluene, ethyl acetate, chloroform) both of which hasten the process. The addition of diammonium hydrogen phosphate, and neutralisation of the liquid by means of ammonia (the extracts as ordinarily prepared have an acid reaction) also have a similar although less pronounced effect.

The crude extract contains phosphates, precipitable by magnesium salts, and albumins, which may be removed by adding an excess of lead acetate, the lead being subsequently removed by passing hydrogen sulphide, and the residual acetic acid by dialysis.

When a limited amount of kaolin is added to the crude extract, adsorption of albumins occurs, but no appreciable amount of invertase is taken up. On the other hand, after the invertase has been purified by adsorption on aluminium hydroxide and subsequent extraction from the adsorbate, kaolin adsorbs it preferentially

and a further purification can thus be effected, the accompanying resins remaining in the mother-liquor.

Invertase is strongly adsorbed by aluminium hydroxide, even from aqueous solution, and still more strongly from an aqueous solution containing, say, 28% of acetone or of alcohol. A study of the fractional adsorption of invertase on aluminium hydroxide shows that at first certain impurities are taken up, and that only after an appreciable amount of aluminium hydroxide has been added does the invertase begin to be adsorbed in large quantities. In the later stages, the amount of invertase adsorbed by a given weight of aluminium hydroxide diminishes asymptotically in such a manner that in preparing the adsorbate for the purpose of purifying the invertase it is often convenient to leave about 10% in the mother-liquor.

The invertase cannot be extracted from the adsorbate by pure water, or by water charged with carbon dioxide. With a concentrated aqueous solution of sucrose, the adsorbate behaves just as though the invertase which it contains were free, and, since the quantity of invertase in a solution is always estimated by means of its activity towards sucrose, this property of the adsorbate affords a means of examining its stability. It is found that a decided loss of activity occurs on keeping. Almost quantitative extraction can be effected by means of 1% aqueous disodium hydrogen phosphate, 1% aqueous diammonium hydrogen phosphate, 0·04% aqueous ammonia, 1% ammonium oxalate, very dilute sodium carbonate, and aqueous pyridine.

It is a curious fact that when the original yeast extract is prepared without the addition of ammonium hydroxide a preliminary purification by precipitation with lead acetate hinders the extraction by ammonia of the invertase from its adsorbate with aluminium hydroxide, whilst if neutral extracts, obtained with the aid of ammonia, be employed a preliminary treatment with lead acetate appears to be necessary to ensure successful extraction by ammonia.

Invertase is adsorbed by normal calcium phosphate ($Ca_3P_2O_8$), but conversion of this into calcium hydrogen phosphate ($CaHPO_4$) renders extraction possible.

A solution in water of invertase which has reached a certain degree of purity gives a precipitate with uranyl acetate. If sufficient uranyl acetate be employed this precipitate contains the whole of the invertase originally present in the solution. Extraction takes place in 0·01*N*-aqueous sodium carbonate.

Using the above facts methods are detailed in the original for the preparation of invertase.

Invertase decomposes gradually in aqueous solution, loss of activity being complete in one and a half years, and fairly quickly in the presence of more than a limited quantity of alcohol or acetone. It undergoes a temporary loss of activity on drying. C. K. I.

Action of Emulsin from Almonds on Lactose in Solution in 85% Ethyl Alcohol. MARC BRIDEL (*Compt. rend.*, 1921, **173**, 501—504).—From the products of the action of emulsin on a

0·2% solution of lactose in 85% alcohol at the ordinary temperature, ethyl β-galactoside was isolated. The lactose is thus first hydrolysed and then the galactoside is synthesised. W. G.

Lead Triaryl, a Parallel to Triphenylmethyl. II. Lead Tri*cyclo*hexyl. ERICH KRAUSE (*Ber.*, 1921, **54**, [*B*], 2060—2066; cf. Krause and Schmitz, A., 1920, i, 197).—The preparation of lead tri*cyclo*hexyl as a crystalline substance the molecular weight of which in dilute solution corresponds exactly with that required by the formula $(C_6H_{11})_3Pb$ places beyond doubt the existence of organo-derivatives of tervalent lead. The substance has the unusual property of uniting with iodine in benzene solution at the ordinary temperature to form lead tri*cyclo*hexyl iodide with such readiness that it may be estimated quantitatively in this manner, whereas when warmed with an excess of iodine it loses a *cyclo*-hexyl group and yields lead di*cyclo*hexyl di-iodide. Since lead tetra*cyclo*hexyl can only be produced with great difficulty, it is obvious that the formation of lead triaryls depends on the molecular volume of the radicle introduced rather than on its chemical nature.

[With G. S. REISSAUS.]—*Lead tri*cyclo*hexyl*, thin, yellow, hexagonal platelets, decomp. 195°, is prepared by the gradual addition of finely-divided lead chloride to a solution of magnesium *cyclo*-hexyl bromide in dry ether; in substance or when dissolved in benzene, it is very sensitive to the action of light, but the dry compound can be preserved indefinitely in the dark. *Lead tri*cyclo*hexyl iodide*, $Pb(C_6H_{11})_3I$, crystallises in long, golden-yellow, rhombic prisms, m. p. 91·7°; it is converted by aqueous potassium hydroxide solution into *lead tri*cyclo*hexyl hydroxide*, which could only be isolated as a white, amorphous powder. *Lead tri*cyclo*hexyl chloride*, pale yellow, slender needles, decomp. about 236°, and *lead tri*cyclo*hexyl bromide*, straw-yellow needles, decomp. about 210°, are also described. *Lead di*cyclo*hexyl di-iodide*, $Pb(C_6H_{11})_2I_2$, crystallises in pale yellow needles, decomp. about 98°, and is somewhat unstable, whereas the corresponding *dibromide* forms pale yellow needles, decomp. about 142°. *Lead tetra*cyclo*hexyl*, colourless, rectangular platelets, which become yellow at 130° and blacken at 160°, is prepared by the protracted action of an ethereal solution of magnesium *cyclo*hexyl bromide on lead tri*cyclo*hexyl bromide. H. W.

Improvements relating to Soluble [Organic] Mercury Compounds. J. D. RIEDEL AKT. GES. (Brit. Pat. 161922).—Hydroxymercurisalicylic anhydride (170 grams), suspended in water, is treated with potassium cyanide (37 grams) and the amorphous mercury compound is rapidly converted into a crystalline mass, which, when a considerable amount of water is present (for example, 800 grams) consists of the potassium salt of the *o*-cyanomercurisalicylic acid. With a lesser quantity of water (500 grams), the product consists of a mixture of this substance with the corresponding *para*-compound, which may be isolated by

extracting the crystalline mass obtained after filtering off the coloured mother-liquor and washing with aqueous alcohol, with about three times its weight of water at 25°, and cooling the extract to 0°, when a woolly mass of crystals separates and is purified by recrystallisation from hot water. The pure ortho-compound forms colourless, short prisms with a satin lustre, soluble in about 25 parts of water at ordinary temperatures with a neutral reaction. The pure para-compound forms oblong tables about four times as soluble in water as its isomeride. The solution has an acid reaction and darkens with ammonium sulphide more rapidly than the ortho-isomeride. Both compounds give with silver nitrate a silver salt of the formula $CN\cdot Hg\cdot C_6H_3(OH)\cdot CO_2Ag$.

G. F. M.

Organo-chromium Compounds. I. Chromium Pentaphenyl Hydroxide. FRANZ HEIN (*Ber.*, 1921, **54**, [*B*], 1905—1938).—A detailed account of investigations, a preliminary notice of which has appeared previously (A., 1919, i, 232). Chromium pentaphenyl bromide, $CrPh_5Br$, is obtained as an orange-brown, amorphous substance by the action of an ethereal suspension of chromic chloride on a well-cooled ethereal solution of magnesium phenyl bromide. The product is doubtless a mixture of substances and the yields are not good; its purification is rendered exceptionally difficult by its sensitiveness towards air, light, rise of temperature, and acids, and by its persistently amorphous nature. With alcoholic mercuric chloride solution, the crude product yields a mercurichloride, $CrPh_5Br,HgCl_2$, which can be purified by repeated extraction with boiling alcohol, under which it melts to a product resembling sealing-wax. The latter appears to be homogeneous, but is still less stable than the crude bromide. From it, it has been found possible with difficulty to prepare the *compound*,

$$2CrPh_5Br,Et_2O,$$

an amorphous powder which softens at about 80° and has m. p. about 100° (decomp.). A similar crude chromium pentaphenyl bromide can be obtained from chromyl chloride and magnesium phenyl bromide in the presence of well-cooled benzene (cf. Sand and Singer, A., 1904, i, 38), but not from chromic oxide. The production of the compound from a derivative of hexavalent chromium renders it probable that the reaction with chromic chloride takes place in accordance with the scheme $4CrCl_3 + 5MgPhBr \longrightarrow CrPh_5Br + 2MgBr_2 + 3MgCl_2 + 3CrCl_2$, which would account for the poor yield of the organochromium product.

The bromine atom of chromium pentaphenyl bromide is displaced with unusual readiness, for example, when its solution in chloroform is agitated with an aqueous suspension of silver oxide, whereby the chromium pentaphenyl hydroxide passes into the aqueous layer. Since the other chromium compounds present in the crude bromide remain dissolved in the chloroform, a ready method of preparing the hydroxide seemed to be indicated; these hopes were not, however, fulfilled, since it was found that the silver oxide also exerted an oxidising action, and that a mixture of

bases resulted which decomposed with extreme readiness and from which it was not possible to prepare solid or crystalline salts with the possible exception of the perchlorate. The strength of chromium pentaphenyl hydroxide inhibits its production by the use of potassium hydroxide in the usual manner, but, by reason of the insolubility of potassium bromide in alcohol, this can be achieved by working with the latter solvent. For this purpose, alcoholic solutions of the crude bromide and potassium hydroxide are mixed, diluted with ether, and filtered from the precipitated potassium bromide; the filtrate is concentrated, and the well-cooled residue is treated with chloroform or anisole to remove excess of potassium hydroxide. The clear solution is shaken with ice-cold water into which the chromium phenyl bases gradually pass and from which *chromium pentaphenyl hydroxide* separates in the form of golden-yellow leaflets or prismatic needles. The substance is best preserved over potassium hydroxide solution (30%) and under diminished pressure. When prepared under these conditions (which correspond with air-drying), the substance loses $2H_2O$ when placed over calcium chloride and a further $2H_2O$ in the presence of phosphoric oxide (in the latter process the colour changes from brownish-orange to a dark olive-brown). Its constitution is therefore expressed by the formula

$$[CrPh_5(OH)_2]OH,2H_2O.$$

The completely dehydrated substance decomposes somewhat readily when preserved at the ordinary temperature, with the production of diphenyl; a similar but slower change occurs with the dihydrate. The anhydrous base and its dihydrate can be re-hydrated to the tetrahydrate. When placed over concentrated sulphuric acid, the substance loses 2% of water and yields an orange-coloured product, the analyses of which give results agreeing with those required by the dihydrate of chromium pentaphenyl hydroxide; this cannot be dehydrated further over phosphoric oxide (the *modification* is termed the β-base). Comparison of the electrical conductivities of chromium pentaphenyl hydroxide, sodium hydroxide, and ammonia in absolute methyl-alcoholic solution proves the former to be a very strong base; in aqueous methyl-alcoholic solution the conductivity of the former does not appear to approach a limiting value with increasing dilution, a peculiarity for which a satisfactory explanation is not at present forthcoming. The ultra-violet absorption spectrum has been measured in absolute ethyl alcoholic solution and found to be closely similar to that of solutions of chromic acid and dichromates, but the absorption is noticeably greater in the case of the base than in those of the acid or salts. H. W.

Physiological Chemistry.

Acidosis. XVII. The Normal and Abnormal Variations in the Acid–Base Balance in the Blood. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1921, **48**, 153—176).—This paper is a review of recent work on the subject of the regulation of the reaction of the blood. For purposes of illustration, a diagrammatic representation is adopted of the different conditions which may arise as the result of variations in the acid–base ratio. These conditions, together with the compensatory measures employed by the body to meet them, are discussed at some length.

Further, the question of the relation of the acid–base balance of the blood to that of the other body-fluids, and the question of the available alkali of the blood, are considered, and a brief reference is made to methods which have been suggested for the determination of the state of the acid–base balance. C. R. H.

The Potassium Content of Normal and some Pathological Human Bloods. VICTOR C. MYERS and JAMES J. SHORT (*J. Biol. Chem.*, 1921, **48**, 83—92).—Figures are given for the amount of potassium present in human serum and whole blood under normal and various pathological conditions. The estimations were made by the cobaltinitrite method, and the precautions essential to the success of the analysis are discussed. C. R. H.

Calcium in the Blood of Children. W. DENIS and F. B. TALBOT (*Amer. J. Diseases Children*, 1921, **21**, 29—37).—By a modification of Lyman's nephelometric method the following results, expressed in mg. of calcium per 100 c.c. of plasma, were obtained: normal adults, 7·2 to 12·1 (average 10); children (8—10 months old) suffering from acute rickets, less than 2 to 8; children (6 months to 4 years) convalescent, 4·5 to 11·2; tetany cases (4—22 months), 1 to 7·7; cases of convulsions without tetany, 3·2 to 8·2; epilepsy cases, 3 to 9; chorea cases, 4·8 and 6; pneumonia cases (6 months to 7·5 years), less than 2 to 12·1. In a number of cases the magnesium was also estimated.

CHEMICAL ABSTRACTS.

The Amount of Amino-acids in Blood. K. DE SNOO (*Diss. Utrecht*, 1920, 130 pp.; from *Physiol. Abstr.*, 1921, **6**, 368).—The amount of nitrogen due to amino-acids in human blood is, on an average, 6·8 mg. per 100 c.c. This amount increases after a protein meal, as also does the amino-acid content of the urine. Absorption of amino-acids probably ceases six hours after a meal. Details of the variation of the amino-acid content of the blood in cases of certain diseases are given. E. S.

Colorimetric Experiments on Tryptophan. V. The Proteins of Immune Sera and their Tryptophan Content. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Zeitsch.*, 1921, **116**, 232—236).—Sera from horses immunised against diphtheria, dysentery,

and tetanus showed an increased content of sera protein due to an increase in the ψ-globulin fraction. The content of tryptophan in each fraction was, however, normal. H. K.

Photosynthetic Processes in the Air, upon the Land, and in the Sea in Relation to the Origin and Continuance of Life on the Earth. Hugo Müller Lecture, delivered before the Chemical Society on June 16th, 1921. BENJAMIN MOORE (T., 1921, **119**, 1555—1572).

Dietary Factors influencing Calcium Assimilation. I. The Comparative Influence of Green and Dried Plant Tissue, Cabbage, Orange Juice, and Cod-liver Oil on Calcium Assimilation. E. B. HART, H. STEENBOCK, and C. A. HOPPERT (*J. Biol. Chem.*, 1921, **48**, 33—50).—The calcium balance of dry and lactating goats is positive on a diet of green oats and negative on one of dry oat straw. It is therefore concluded that the former diet contains a dietary factor which facilitates calcium assimilation. The same factor is present in cod-liver oil but absent in raw or dried cabbage. Experiments with orange juice did not lead to consistent results (cf. also Steenbock and Hart, A., 1913, i, 550; Meigs, Blatherwick, and Cary, A., 1920, i, 203). E. S.

The Behaviour of the Residual Nitrogen of Egg-white and of Yolk on Incubation. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 12—14).—After removal of all substances precipitable by boiling dilute acetic acid and by tannic acid solution, the author determined the total residual nitrogen in the filtrate by Kjeldahl's method, the nitrogen in the fraction still precipitable by phosphotungstic acid by Kjeldahl's method, and the amino-nitrogen in the final filtrate by van Slyke's method. Fresh eggs contain very little residual nitrogen or amino-nitrogen, but as incubation proceeds there is a steady increase of residual nitrogen up to fourteen days. H. K.

Behaviour of Dextrose added to the White of Eggs during Incubation. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 22—27).—The normal content of dextrose in eggs after three days' incubation is 0·43% in the egg-white and 0·2% in the yolk. Addition of dextrose to the white of fresh eggs followed by incubation for three days causes a marked disappearance of dextrose from the egg-white, but not from the yolk. Dextrose appears therefore to be a source of the lactic acid produced. H. K.

The Formation of *d*-Lactic Acid in the Animal Organism. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 1—11).—Quantitative experiments on eggs show that the *d*-lactic acid content is very small and of the order 0·006% in egg-white and 0·01% in the yolk. The lactic acid content of unfertilised is less than that of fertilised eggs, and, as incubation proceeds, the lactic acid reaches its maximum on the fifth day and becomes very small at the end of a fortnight. H. K.

The Influence of the Addition of Dextrose and Alanine to Egg-white on the Formation of *d*-Lactic Acid during Incubation. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 15—21).—Dextrose and alanine were separately added to the white of an egg and the egg incubated for three days. Alanine had no marked effect on the lactic acid content of egg-white or yolk, but dextrose produced an increase in the lactic acid content of egg-white somewhat less than 100%. H. K.

The Formation of Sarcolactic Acid in the Animal Organism. The Formation of *d*-Lactic Acid by the Autolysis of Hen's Eggs. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 28—39).—The lactic acid content of egg-white undergoing autolysis is independent of time, but that of the yolk increases considerably and eventually falls off. If dextrose is added to yolk, the lactic acid shows an enormous increase, whilst that of the egg-white is unchanged. Alanine has no effect in either case. During autolysis, an enzyme present in the yolk, but not in the egg-white, has the power of converting dextrose into lactic acid. H. K.

Chemical Composition of the Egg-shell of the Silkworm Moth. MASAJI TOMITA (*Biochem. Zeitsch.*, 1921, **116**, 40—47).—The egg-shell of the silkworm moth is composed of protein and not of chitin. On hydrolysis with acids and separation of the amino-acids by the standard methods, 40% of the constituent amino-acids was isolated. Glycine, 13·7%, and tyrosine, 11·2%, were present in the largest proportion. H. K.

Can the Chloridion of Ringer Solution be Replaced by other Ions with the beating Frog's Heart? E. R. O. FINCKH (*Biochem. Zeitsch.*, 1921, **116**, 262—265).—An isolated frog's heart continues to beat when all chloridion is replaced by bromidion. The substitution by the iodide ion or by the nitrate ion exerts a harmful effect owing to formation of iodine or nitrite. H. K.

Conditions for the Precipitation of the Wassermann Reaction Antigen (Heart Extract). RUDOLF MÜLLER (*Biochem. Zeitsch.*, 1921, **116**, 215—223).—When an alcoholic extract of ox-heart is added to sodium chloride solutions of various concentrations, a colloidal solution is primarily obtained, further addition of the alcoholic solution leading to precipitation. The higher the initial concentration of the saline solution the smaller the quantity of the alcoholic heart-extract necessary to produce precipitation. H. K.

The Selective Absorption of Potassium by Animal Cells. I. Conditions Controlling Absorption and Retention of Potassium. PHILIP H. MITCHELL and J. WALTER WILSON (*J. gen. Physiol.*, 1921, **4**, 45—56).—The potassium content of the muscles of frogs decreases by 8 to 15% during perfusion with a potassium-free Ringer solution, but this loss may be due entirely to the presence of a potassium-free medium. There is no additional

loss of potassium if the muscle is stimulated during the perfusion, but a larger loss occurs if stimulation is carried so far as to cause loss of irritability. Probably this is connected with the fact that a contracting muscle more readily takes up rubidium and cæsium than a resting one. W. O. K.

Chemical and Physical Properties of Muscle and Muscle Extracts. VII. Fats, Cholesterol, and Lipoids in the Extract from Striped Muscle of Dogs. G. QUAGLIARIELLO (*Arch. internat. Physiol.*, **16**, 239—250; from *Chem. Zentr.*, 1921, iii, 568).—The extract was obtained from the muscle of fasting dogs, using a Buchner press. After separation of fat by centrifuging, the extract was warmed with an equal volume of 1% sodium chloride for thirty minutes at 45° and then placed in an ice-chest for twenty-four hours, whereby myosin separated in granular form. This was removed by centrifuging and the myoprotein remaining in solution separated by coagulation. The myosin was examined quantitatively for ash, total nitrogen, total fatty acids, unsaponifiable fat (cholesterol), and lipoid phosphorus. In the case of the myoprotein, total nitrogen, total acid, and cholesterol were estimated. Of the total fatty acids and cholesterol in the fat-free extract, 90% occurred in the myosin granules. Of the fatty acids in myosin, half is associated with phospholipoids. The author concludes that the myosin granules (and consequently the fibrillæ) consist of lipoid substances, although no constant relationship was found between the total nitrogen and the total fatty acids of the myosin granules, as might be expected from this hypothesis (cf. A., 1913, i, 1132). G. W. R.

Do Subminimal Stimuli influence the Course of Chemical Changes in Muscle? JAKOB K. PARNAS and EMILIA LASKA-MINTZ (*Biochem. Zeitsch.*, 1921, **116**, 59—70).—Contrary to the findings of Heidenhain and Gottschlich (*Pflüger's Archiv*, 1894, **55**, 355), the subminimal stimulation of frog's muscle failed to produce any increase in the normal lactic acid content or in the degree of acidity. The lactic acid was estimated by Parnas's modification of the method of von Fürth and Charnass (*Zentr. Physiol.*, 1915, **30**, 1), an important simplification being the extraction of the lactic acid by grinding the muscle with quartz sand and saturated ammonium sulphate at −10°. H. K.

Carbohydrate Metabolism of Isolated Amphibian Muscle. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 71—88; cf. A., 1914, i, 772).—Details are given for the estimation of the carbohydrate content of 0·5 to 1·5 grams of muscle. Using this method, the author has investigated the relation between the carbohydrate consumption of muscle stimulated to maximum contraction several thousand times and the work done by it. The efficiency of the gastrocnemius is 35% and the sartorius 50%. The latter value agrees with that found by Hill (*Ergebnisse Physiol.*, 1916, **15**, 341). H. K.

The Carbohydrate Metabolism of Isolated Amphibian Muscle. The Exchange in the Muscle of Pancreas-diabetic Animals. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 89—101; cf. A., 1914, i, 772).—Experimental glycosuria was produced by removal of the pancreas from water-frogs. The carbohydrate consumption of the resting muscle and the amount of lactic acid formed in resting muscle and in heat-rigor muscle was the same as that of normal muscle. The same applies under anærobic conditions. The oxygen consumption of the muscle of the pancreas-free frog was the same as that of normal muscle, but the mechanical efficiency was somewhat less. The metabolism of the muscles of diabetic animals is thus identical with that of normal muscle. H. K.

Mechanical Efficiency of the Combustion Processes occurring in Isolated Amphibian Muscle. JAKOB K. PARNAS (*Biochem. Zeitsch.*, 1921, **116**, 102—107).—By means of an apparatus which is pictured and fully described, the oxygen consumption of the gastrocnemius muscle of the frog, whilst undergoing a great number of contractions, was measured over a period of several hours. The work done by the muscle compared with that calculated from the oxygen consumption showed a mechanical efficiency of 44%. This agrees closely with the efficiency determined from the consumption of carbohydrate by the sartorious muscle. The only source of energy in isolated muscle is therefore the carbohydrate. H. K.

Proteins of the Muscle of *Haliotis gigantea*, Gmelin. EIJI TAKAHASHI (*J. Chem. Soc. Japan*, 1921, **42**, 537—545).—Crushed pieces of the muscle of the ear-shell, *Haliotis gigantea*, were boiled with water, the insoluble part was treated with alcohol and ether and dried; it contained water 4·02%, ash 6·40%, and total nitrogen 14·236%. One hundred and twenty grams of the dried sample were hydrolysed by boiling with 360 grams of 25% sulphuric acid during ten hours and the following monoamino- and diamino-acids were isolated (in grams): cystine 4·3, tyrosine 5·6, glutamic acid 12·4, alanine 1·2, leucine 18·0, proline 2·7, serine 2·3, aspartic acid 3·8, arginine 6·4, hystidine 0·4, and lysine 3·4 grams. Glycine was not present, and the presence of phenylalanine and valine is doubtful. K. K.

The Distribution of Urea in the Organism. K. L. GAD-ANDRESEN (*Biochem. Zeitsch.*, 1921, **116**, 266—302).—A complete study of the amount of urea in the various parts of the body. The distribution coefficient of urea between plasma and corpuscles and between Ringer solution and corpuscles is between 0·72 and 0·8. Between plasma and the various secretions the coefficient is unity, whilst between plasma and water-free fat it is 0·07. The concentration of urea is the same in all tissues and in the blood, with the exception of the fatty tissues. The concentration of ammonia is the same in the blood, the secretions, and the various organs. H. K.

The Metabolism of Amphibian Larvæ. JAKOB K. PARNAS and ZOFIA KRASINSKA (*Biochem. Zeitsch.*, 1921, **116**, 108—137).—The oxygen consumption of the larvæ of frogs was determined from the moment of fertilisation and on through the early stages of growth. The influence of the proportion of oxygen, and of the presence of urethane, was also investigated. In general, over the whole period of growth there is a progressive increased consumption of oxygen, although over short periods of evolution of the larvæ the oxygen consumption may be constant. The paper is fully illustrated by graphs and figures. H. K.

The Fat of *Caballus equus*. A. HEIDUSCHKA and A. STEINRUCK (*J. pr. Chem.*, 1921, **102**, 241—266).—The material under investigation was a mixed product obtained from the various fatty tissues of the horse; it had m. p. 32·3°, d^{15} 0·9224, d^{25} 0·9135, n_D^{40} 1·4617, acid value, 2·62, saponification value, 203·95, Reichert-Meissl value, 0·417, Polenske value, 0·375, iodine value, 75·17, acetyl value, 14·02, saponification value after acetylation, 6·93.

The liquid fatty acids contain, in addition to oleic acid, 7·34% of linolic acid and 1·61% of linolenic acid. Farnsteiner found 9·9% of linolic acid, but the difference is explained by the fact that he calculated the content from the iodine value of the unsaturated acids obtained from the kidney fat, whereas the author employed an average sample of the total fat. Varrentrapp's method for the separation of the solid and liquid acids does not give exact values; better results are obtained by the precipitation of an ethereal solution of the total fatty acids with alcoholic lead acetate solution.

The solid fatty acid does not consist of heptadecoic acid, but of a mixture of palmitic and stearic acids; this result is confirmed by three independent methods of analysis.

The total fatty acids are composed of linolenic acid 1·69%, linolic acid, 6·68%, oleic acid, 55·24%, stearic acid 6·82%, palmitic acid 29·47%. In addition, 0·426% of unsaponifiable matter, mainly cholesterol, is present. H. W.

Glycerides of Goose Fat. CONRAD AMBERGER and KARL BROMIG (*Pharm. Zentr.-h.*, 1921, **62**, 547—548).—Goose fat when kept for some time deposits about 15% of solid fat (iodine number, 52·5) containing α-stearodipalmitin, m. p. 57·4°, and β-stearodipalmitin, m. p. 63·0°; 100 c.c. of ether at 15° dissolve 1·32 grams of the former and 0·90 gram of the latter. The liquid portion of the fat (iodine number 77·0) consists chiefly of triolein, and both solid and liquid portions contain a quantity of oleodipalmitin, m. p. 33·5°. W. P. S.

Chemical Investigation of Mutton-bird Oil. I. C. L. CARTER (*J. Soc. Chem. Ind.*, 1921, **40**, 220T).—Mutton-bird oil is extracted from the stomach of an Australian petrel, *Aestrelata lessoni*. It resembles sperm oil very closely in its physical and chemical properties. The alcohols obtained by saponification of the oil consist chiefly of cetyl alcohol, and the greater portion of the mixed fatty acids consists of oleic acid. There is evidence of the presence of acids of the linolic or linolenic series. W. G.

Chemical Study of (I), certain Pacific Coast Fishes; (II), the California Sardine (*Sardinia cœrulea*). D. B. Dill (*J. Biol. Chem.*, 1921, **48**, 73—82, 93—103).—Large variations were found in the fat content of the fishes studied. These variations could not, usually, be correlated with any other factor, although in many cases the maximum fat content was found in the summer months. E. S.

Formation and Excretion of Hippuric Acid in Man. I. Snapper (*Nederl. Tidschr. Geneesk.*, 1920, **65**, 3044; from *Physiol. Abstr.*, 1921, **6**, 377).—Hippuric acid in amounts up to 300 mg. daily was found in the urine of persons on a milk diet. The source of the benzoic acid necessary for its formation is probably phenylalanine, produced by the digestion of proteins. In men with normal kidneys, 5 grams of sodium benzoate were almost completely excreted in the form of hippuric acid within twelve hours. From a study of certain pathological cases the conclusion is drawn that the glycine depot of the body is not dependent on the bile secretion. E. S.

Amino-nitrogen in the Urine as indicated by the Formol Method. C. Ciacco (*Arch. sci. med.*, 1920, **43**, 177—181).—The author considers that the amino-nitrogen indicated by the formol method in urine is not present in the form of simple amino-acids, but as more or less complex polypeptides. The discordant results commonly obtained are thus explained, since polypeptides are partly precipitated by salts of heavy metals or by phosphotungstic acid. In order to study the elimination of the more or less complex protein fragments in various pathological conditions, it is suggested that the formol method should be applied (*a*) after hydrolysis of the urine without any preliminary treatment, (*b*) after treatment with tannin and lead acetate, or with mercuric acetate, and (*c*) after hydrolysis of the filtrate obtained by precipitation with these substances. Chemical Abstracts.

The Local Anæsthetic Properties of Benzoylcarbinol. A. M. Hjort and C. E. Kaufmann (*Proc. Soc. Exp. Biol. Med.*, 1920, **17**, 79—80).—Benzoylcarbinol possesses local anæsthetic properties which in general are superior to those of benzyl alcohol, α-methylbenzyl alcohol, or phenylethyl alcohol. Benzoylcarbinol is less irritant to the body-tissues than these compounds, and is the most stable of the series. Its solubility in water is sufficient to make it a practicable local anæsthetic. Chemical Abstracts.

Methylation in the Animal Organism. I. Methylation of Pyridine in the Organism of the Rabbit. Masaji Tomita (*Biochem. Zeitsch.*, 1921, **116**, 48—54).—Contrary to the findings of Abderhalden and his co-workers, rabbits on various diets can convert pyridine to a small extent into methylpyridine, which was isolated as the platinum salt. H. K.

Methylation in the Animal Organism. II. The Site of the Methylation of Pyridine in the Animal Organism. Masaji Tomita (*Biochem. Zeitsch.*, 1921, **116**, 55—58).—Extirpation of

the spleen or pancreas in frogs has no influence on the production of methylpyridine, whilst removal of the liver completely inhibits it. In dogs, removal of the testicles or spleen has no influence on the production of methylpyridine. The methylation is assumed to take place in the liver, but experiments with isolated organs have not so far been successful. H. K.

Biological Action of Proteinogenous Amines. A Contribution to the Question of the Acetonitrile Reaction. O. WUTH (*Biochem. Zeitsch.*, 1921, **116**, 237—245).—Hunt (A., 1905, ii, 847) showed that the toxicity to mice of acetonitrile is greatly diminished by previous administration of thyroid substance. The author finds that tyramine and di-iodotyramine can likewise protect mice against acetonitrile. Histamine is, however, without action. H. K.

The Toxicity of Acids to Infusoria. II. and III. M. E. COLLETT (*J. Exp. Zool.*, 1921, **34**, No. 1; from *Physiol. Abstr.*, 1921, **6**, 353, 354).—II. The addition of hydrochloric acid to solutions of organic acids does not yield conclusive evidence as to the toxicity of the molecule. Mixtures of certain acids (formic, acetic, butyric, valeric, benzoic, salicylic, with Paramœcium and Euplotes, and citric with Euplotes only) with their sodium salts are more toxic than can be accounted for by the P_H of the mixture or the toxicity of the salts. This seems to indicate that the molecules of these acids are in themselves toxic. There is no evidence of toxicity of the anion or the molecule in lactic, succinic, or tartartic acid at the concentrations used. The relative toxicity of $0{\cdot}01M$-solutions of the sodium salts is as follows: Paramœcium—salicylate, benzoate, tartrate, succinate, citrate, formate, acetate, butyrate, valerate, chloride, lactate; Euplotes—citrate, salicylate, benzoate, tartrate, succinate, formate, chloride, acetate, butyrate, valerate, lactate.

III. Length of life in solutions of various acids is extended by the addition of inorganic chlorides. The acids tested fall into two groups: the first includes hydrochloric, formic, acetic, succinic, lactic, tartaric, citric; the second butyric, hexoic, benzoic, salicylic, phenylacetic. The relative antagonistic power of the chlorides is set out. Sodium chloride increases the antagonistic power of barium and magnesium chlorides against all acids, but that of calcium and strontium chlorides only against acids of the second group. The action of the salts is probably double. Each has some influence on phase reversal, and thus on the rate of penetration of the acid; and each also stabilises the cell colloids against the swelling or coagulative action of the H-ion. E. S.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation Process for the Production of Acetone, Alcohol, and Volatile Acids from Maize Cobs. W. H. Peterson, E. B. Fred, and J. H. Verhulst (*J. Ind. Eng. Chem.*, 1921, **13**, 757—759).—When maize cobs are heated under a pressure of 20 lb. per square inch with about four times their weight of water and 8% of their weight of sulphuric acid, they yield from 25 to 30% of reducing sugars, chiefly xylose. The crude xylose syrup obtained is fermented readily and almost completely by *Bacillus acetoethylicum*; 100 lb. of maize cobs yield 2·7 lb. of acetone, 6·8 lb. of alcohol, and 3·4 lb. of formic and acetic acids. During the fermentation an excess of calcium carbonate must be present to neutralise the acids as they are formed. W. P. S.

The Manufacture of Nitrates by the Biochemical Oxidation of Ammonia. E. Boullanger (*Ann. Inst. Pasteur*, 1921, **35**, 575—602).—A description of large-scale laboratory experiments designed to determine the best conditions for the preparation of nitrates by the biochemical oxidation of ammonium salts in solutions percolating through peat or some other material charged with nitrifying organisms.

In the first stages a 0·25% solution of ammonium sulphate should be used percolating at the rate of 20—40 litres per cub. metre of peat per day. When the organisms have spread throughout the mass, this amount may be gradually increased to 200 litres of 0·75% solution. The presence of nitrates at the commencement checks the multiplication of the nitrifying organisms. Later on, ammonium nitrate, obtained by the interaction of the calcium nitrate previously formed and ammonium carbonate, may be used. It is preferable to pass the solution repeatedly through the same peat after adding each time a fresh amount of ammonium nitrate, and in this way it is possible to bring the concentration of the calcium nitrate up to 120 grams per litre without harm to the nitrifying organisms.

The peat may advantageously be replaced by pozzolani or volcanic scoriæ as supports of the nitrification. W. G.

The Decomposition of Pyruvic Acid by Various Fungi. T. Nagayama (*Biochem. Zeitsch.*, 1921, **116**, 303—306).—Six species of moulds were able to decompose pyruvic acid with production of acetaldehyde. The proportion of the latter was increased by addition of sodium or calcium sulphite. H. K.

Effect of Salt Proportions and Concentrations on the Growth of *Aspergillus niger*. C. M. Haenseler (*Amer. J. Bot.*, 1921, **8**, 147—167).—When *Aspergillus niger* is grown on nutrient solutions containing potassium dihydrogen phosphate, calcium nitrate, and magnesium sulphate, increase in the total concentration

of solutions containing the same proportions of salts produces a corresponding increase in yield. The yield is approximately proportional to the amount of nitrate present in the culture, although the partial concentrations of the other two salts can be varied within wide limits without affecting the yields. Calcium nitrate is preferable to sodium nitrate as a source of nitrogen. In cultures with constant proportions of salts and total salt-concentrations, but with sugar-concentrations varying between 1 and 8 atmospheres, the yields of fungus are very nearly proportional to the sugar-concentrations of the cultures. CHEMICAL ABSTRACTS.

Influence of Temperature on the Utilisation of Dextrose in the Development of *Aspergillus niger*. ÉMILE F. TERROINE and RENÉ WURMSER (*Compt. rend.*, 1921, **173**, 482—483).—For a given medium, the ratio of dry weight of mycelium formed to dextrose consumed in the growth of *Aspergillus niger* is independent of the temperature over the range 22° to 38°. W. G.

Formation of Vitamin-*A* in Living Plant-tissues. KATHARINE HOPE COWARD and JACK CECIL DRUMMOND (*Biochem. J.*, 1921, **15**, 530—539).—Dried seeds are generally deficient in vitamin-*A*, and, unlike that of the anti-scorbutic vitamin, the amount is not increased on germination. The formation of vitamin-*A* is closely dependent on the presence of chlorophyll; it is formed in green leaves from inorganic salts in water-cultures, but not in etiolated leaves or in mushrooms. Vitamin-*A* is apparently not associated with proteins, but may be removed with fat by solvents, and appears in the unsaponifiable fraction of the latter. G. B.

The Function of Calcium in the Nutrition of Seedlings. RODNEY H. TRUE (*J. Amer. Soc. Agron.*, 1921, **13**, 91—107).—Seedlings were grown in water culture solutions under laboratory conditions. Injury resulted to plants grown in pure water, for water represents a partial ionic vacuum to roots and tends to establish an equilibrium with cell contents by the withdrawal of ions from the plant. Any one pair of ions will not fully overcome the injurious action, but it is largely overcome by salts yielding the calcium ion; to a less degree it is overcome by those yielding magnesium ions and but slightly or not at all by those carrying potassium or sodium ions. Calcium chloride, carbonate, and nitrate are most abundantly absorbed, whilst calcium sulphate is absorbed by plants which grow on sandy and acid lands. An increase in the number of kinds of nutrient ions present in the solution increases the absorption of electrolytes. Potassium ions when offered in a simple solution are neglected, but when accompanied by calcium ions are absorbed. Calcium ions make potassium physiologically available, whilst a less striking action by potassium ions exists for producing absorption of calcium ions. As the variety of ions present in the solution is increased, the importance of rather sharply marked proportional relations becomes distinctly less than in simpler solutions. The presence of a certain minimal quantity of

calcium ions is probably the most striking single chemical condition of the solution. Doubtless, the physiology of the cell is the basis for an understanding of special services performed by the calcium ion. CHEMICAL ABSTRACTS.

Effect of Ammonium Sulphate on Plants in Nutrient Solutions supplied with Ferric Phosphate and Ferrous Sulphate as Sources of Iron. LINUS H. JONES and JOHN W. SHIVE (*J. Agric. Res.*, 1921, **21**, 701—728).—Wheat plants grown in the twenty selected Tottingham solutions (cf. *Physiol. Res.*, 1914, [v], **1**, 133) invariably produced a marked decrease in the hydrogen-ion concentrations of the solutions. Plants grown in similar solutions, in which ammonium sulphate was substituted for the potassium nitrate in equivalent osmotic concentrations, invariably caused an increase in the hydrogen-ion concentrations of these solutions during the early stages of growth.

Ferric phosphate, in the quantities used (0·83 mg. of iron per litre), was not sufficiently available in the Tottingham solutions to supply the needs of the plants for iron, but it was readily available to the plants in the solutions containing ammonium sulphate. Ferrous sulphate, used in the same proportion as regards iron, was sufficiently available in the Tottingham solutions to satisfy the needs of the plant for iron. The solutions containing ammonium sulphate with this form of iron in quantities of more than 0·01 mg. of iron per litre were very toxic to the plants, the degree of toxicity increasing with the amount of iron added to the solutions.

The nature of the nutrient solution with respect to the salt constituents and hydrogen-ion concentration appears to determine the availability and the efficiency of a given iron salt for plant growth. W. G.

Oxalic Acid Content of Young Leaves in Spring Foliage. ARMINIUS BAU (*Zeitsch. techn. Biol.*, 1921, **8**, 151—155; from *Chem. Zentr.*, 1921, iii, 175—176).—The spring foliage of *Sambucus nigra*, *Cratægus oxyacantha*, *Aesculus hippocastanum*, and barley gave small but measurable amounts of total and water-soluble oxalate. The total oxalate, calculated as oxalate-ion in the dry matter, varied from 0·495% in the young shoots of *Sambucus*, gathered in the afternoon, to 0·03% in the young leaves of barley. The amount of water-soluble oxalate, where estimated, was approximately one-third of the total oxalate. In the case of *Sambucus*, an increase in total oxalate content was observed from early morning to late afternoon. G. W. R.

The Chemical Constituents of Green Plants. XIII. On the Volatile Basic Substances of Green Plants. HARTWIG FRANZEN, ADOLF WAGNER, and ARTUR SCHNEIDER (*Biochem. Zeitsch.*, 1921, **116**, 208—214).—Out of twenty-eight plants examined all contained volatile basic substances; in the case of thirteen ammonia was identified. The amount of other volatile bases is very minute, even when employing a kilo. of starting material. H. K.

Significance of "Lignin" Colour Reactions. ERNEST C. CROCKER (*J. Ind. Eng. Chem.*, 1921, **13**, 625—627).—The colour reaction obtained when wood is treated with phloroglucinol, *p*-nitroaniline, etc., is not due to the lignin, but to the traces of an aldehyde which usually, if not always, accompany the lignin; one aldehyde, coniferaldehyde, appears to predominate in wood, vanillin or furfuraldehyde occurring in small quantity only. Certain non-aldehydic substances which are known to yield colour reactions similar to those of " lignin " are shown to contain traces of aldehydes which are responsible for the colour formation. In the case of oil of cloves and oil of sassafras, the aldehyde present appears to be identical with that found in wood. Mäule's reaction (production of a red coloration when wood is treated successively with permanganate, dilute hydrochloric acid, and ammonia) is obtained principally with deciduous woods, and may afford a means of distinguishing these woods from coniferous woods, since the latter yield only a faint brown coloration. W. P. S.

Methods of Extracting and Concentrating Vitamins-*A*, -*B*, and -*C*, together with an Apparatus for Reducing Milk, Fruit Juices, and other Fluids to a Powder without Destruction of Vitamins. J. F. MCCLENDON (*J. Biol. Chem.*, 1921, **47**, 411—420).—The essential features of the methods are: the use of high pressure in the extraction of vitamin-*A* from dried green leaves or fruit skins moistened with 95% alcohol; the similar extraction, using 80% alcohol, of vitamin-*B* from wheat germ or yeast, followed by the separation of resinous and lipoid material by acidification up to the isoelectric point of these colloids; and the removal of sugar from the vitamin-*B* extract and also from fruit juices containing vitamin-*C* by fermentation with yeast. The extracts so obtained are concentrated by a spray process in which hot flue gases meet a descending spray of the extract. Oxygen is excluded from the flue gases by regulation of the combustion of the furnace.

E. S.

The Effect of Heat and Oxidation on the Antiscorbutic Vitamin. R. ADAMS DUTCHER, H. M. HARSHAW, and J. S. HALL (*J. Biol. Chem.*, 1921, **47**, 483—488).—The antiscorbutic vitamin in orange juice resists half an hour's boiling at 100° in a reflux apparatus, but is partly destroyed by hydrogen peroxide, especially on warming (cf. Delf, A., 1920, i, 460). G. B.

Carrageen (*Chondrus crispus*). II. The Occurrence of Ethereal Sulphates in the Plant. PAUL HAAS (*Biochem. J.*, 1921, **15**, 469—476).—The colloidal hot water extract consists of a substance more soluble in cold water and giving thick, viscous solutions, and one more soluble in hot water, producing solutions which gelatinise on cooling. The latter is the calcium salt of an ethereal sulphate of which the calcium is freely ionised. Sulphate ions cannot be shown to be present until after hydrolysis. This is why the high ash content of carrageen (14·6%) cannot be reduced by dialysis. G. B.

Manganese in Commonly Grown Legumes. J. S. JONES and D. E. BULLIS (*J. Ind. Eng. Chem.*, 1921, **13**, 524—525).—The following quantities of manganese, expressed as milligrams per kilo of air-dried substance, were found in various leguminous plants:—Vetch, 42; red clover, 33; Alsike clover, 68; lucerne, 23; field peas, 33; sweet clover, 27; white clover, 34. The leaves contained much more manganese than did the other parts of the plants, a fact which supports the theory that the primary function of the manganese is catalytic. W. P. S.

The Presence of a Glucoside Decomposable by Emulsin in Two Species of *Melampyrum*. MARC BRIDEL and (MLLE) MARIE BRAECKE (*Compt. rend.*, 1921, **173**, 414—416).—*Melampyrum arvense*, L., and *M. pratense*, L., each contain an apparently lævorotatory glucoside which is decomposed by emulsin, giving reducing sugars and a black, insoluble compound. It is suggested that this glucoside may be identical with aucubin, a glucoside found in *Aucuba japonica*, L. W. G.

The Saponarin in *Mnium cuspidatum*. ANTOINE KOZLOWSKI (*Compt. rend.*, 1921, **173**, 429—431).—The cellular juice of the stem and leaves of *Mnium cuspidatum* contains, in solution, a colourless substance which gives all the reactions of saponarin. Its presence could not, however, be detected in other species of *Mnium* or in other mosses. W. G.

The Chemical Composition of Peanut Oil. GEORGE S. JAMIESON, WALTER F. BAUGHMAN, and DIRK H. BRAUNS (*J. Amer. Chem. Soc.*, 1921, **43**, 1372—1381).—Two samples of peanut oil were examined, but in neither case was there any indication of the presence of hypogæic acid. The compositions of the two samples were:—unsaponifiable matter 0·2, 0·3%; glycerides of oleic acid, 52·9, 60·6%; of linolic acid, 24·7, 21·6%; of palmitic acid, 8·2, 6·3%; of stearic acid, 6·2, 4·9%; of arachidic acid, 4·0, 3·3%, and of lignoceric acid, 3·1, 2·6% respectively. W. G.

Constituents of *Pelvetia Wrightii*, Yendo. KINSUKE KONDÔ (*J. Chem. Soc. Japan*, 1921, **42**, 537—545; cf. this vol., i, 387). K. K.

The Cellulose Content of Spruce Wood. P. KLASON (*Svensk Pappers Tidning*, 1921, **24**, 7; cf. A., 1920, i, 148).—By continuing the digestion of spruce wood for ten to twenty days, the following revised analytical results were obtained: cellulose free from pentosans, 53%; hemicellulose, 15%; lignin, 30%; other substances, 2%. CHEMICAL ABSTRACTS.

Organic Chemistry.

Petrol prepared from Rape Oil. ALPHONSE MAILHE (*Compt. rend.*, 1921, **173**, 658—660).—When rape oil is passed over a copper–aluminium catalyst at 550—650°, it gives a gas, burning with a very luminous flame and consisting of olefines and paraffins, together with some carbon monoxide and dioxide, and a liquid from which two fractions can be obtained by distillation. If these two lighter fractions are hydrogenated over reduced nickel at 180°, they give a mixture of aromatic and cyclic hydrocarbons.

W. G.

Hydrogenation of Acetylene for the Preparation of Fuel Oils. KEIJI ODA (*J. Chem. Ind. Japan*, 1921, **24**, 1161—1166).—The catalyst was prepared by reducing a mixture of nickel and mercury oxides in a current of hydrogen. Over this catalyst a mixture of equal volumes of purified acetylene and hydrogen was passed slowly at 25—35°. A light oil, consisting of ethylenic hydrocarbons, and a heavy oil, b. p. 200—300°, which remained with the catalyst, were obtained, the total yield being 51·7% of the acetylene.

K. K.

Preparation of Tetrachloroethane and Trichloroethylene from Acetylene and Chlorine. SADAO IGI (*J. Chem. Ind. Japan*, 1920, **23**, 1217—1237).—For the preparation of tetrachloroethane from acetylene and chlorine, the use of antimony pentachloride as a catalyst is desirable, but difficulties arise in the decrease of the absorptive power of the catalyst, in its recovery, and in the danger of explosions. Trichloroethylene is prepared in 84% yield by boiling tetrachloroethane (100 parts) with calcium hydroxide (60 parts) and water (50 parts).

CHEMICAL ABSTRACTS.

Preparation of Methyl Bromide. WILHELM STEINKOPF and GUSTAV SCHWEN (*J. pr. Chem.*, 1921, **102**, 363—364).—The addition of bromine to a mixture of phosphorus and methyl alcohol at the ordinary temperature (Steinkopf and Frommel, A., 1905, i, 501) sometimes results in the production of flame. This danger may be avoided and the yield of methyl bromide, calculated on the bromine used, increased to 77% if the methyl alcohol is boiled for about fifteen minutes before the addition of bromine and gentle boiling maintained while the bromine is being added. Methyl bromide is thus obtained far more cheaply than by Bygdén's method (A., 1911, i, 413).

T. H. P.

The Dimorphism of Potassium Ethyl Sulphate. DALZIEL LLEWELLYN HAMMICK and JOHN MYLNE MULLALY (T., 1921, **119**, 1802—1806).

The Liver Lecithin. P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1921, **48**, 185—196).—Liver lecithin, purified by means of the cadmium chloride compound, yields on hydrolysis two saturated and two unsaturated fatty acids. The former are palmitic and stearic acids, whilst, of the latter, one gives stearic and the other arachidic acid on reduction. The degree of unsaturation of the unsaturated acids has not been determined; the one yielding arachidic acid on reduction appears, however, to form an octabromide. The presence of four different acids suggests that liver lecithin is a mixture of different lecithins. This is confirmed by molecular-weight determinations of hydrolecithin, $C_{44}H_{90}O_9NP$, obtained by Paal's method, for which the boiling-point method yielded values of 810 and 700 (cf. A., 1920, i, 788). E. S.

Preparation of Methyl Mercaptan. F. ARNDT [with E. MILDE and G. ECKERT] (*Ber.*, 1921, **54**, [*B*], 2236—2242).—S-*Methyl*iso*thiocarbamide sulphate*, needles, m. p. 244° (decomp.), is prepared conveniently in about 90% yield by gently warming an aqueous solution of thiocarbamide with methyl sulphate until the first violence of the action subsides and subsequently evaporating the solution until most of the solvent is eliminated. It is decomposed when warmed with 5*N*-sodium hydroxide solution into cyanamide (which immediately becomes polymerised to dicyanodiamide) and methyl mercaptan, which is obtained pure after being washed with a little dilute sulphuric acid and dried with calcium chloride; methyl mercaptan has b. p. 6°, d^0 0·894.

S-*Methyl*iso*thiocarbamide*, SMe·C(:NH)·NH_2, is readily prepared by the action of methyl mercaptan on cyanamide in well-cooled, anhydrous ether; it crystallises in colourless leaflets, m. p. 79° after softening at 75°, becoming decomposed thereby into methyl mercaptan and dicyanodiamide. It can be preserved unchanged in closed vessels in an ice-chest for one to two days, but gradually becomes decomposed with formation of dicyanodiamide. Previous failures to isolate the compound from its salts are not due to inherent instability of the substance, but to the use of solvents of unsuitable boiling-point; the isolation is conveniently effected from the hydrochloride and sodium methoxide in absolute methyl alcoholic solution. H. W.

Some Derivatives of Monothioethylene Glycol. GEORGE MACDONALD BENNETT and EDITH MURIEL WHINCOP (T., 1921, **119**, 1860—1864).

Dichloroacetates and Chlorobromoacetates from αβ-Dichlorovinyl Ethyl Ether. HOLLAND CROMPTON and PHYLLIS MARY TRIFFITT (T., 1921, **119**, 1874—1875).

Anhydrides of the Higher Aliphatic Fatty Acids. D. HOLDE and IDA TACKE (*Chem. Zeit.*, 1921, **45**, 949—950; 954—956; cf. Holde and Smelkus, A., 1920, i, 811; Holde and Tacke, A., 1920, i, 811).—The pure anhydrides of the fatty acids of linseed oil can be prepared in 92·4% yield by heating the mixed fatty acids

with two and a half times the theoretical quantity of acetic anhydride at 140—160°, removal of acetic acid and unchanged acetic anhydride by distillation of the product from a boiling-water bath under 14 mm. and finally under 1—2 mm. pressure, agitation of the solution of the residue in light petroleum with sodium carbonate solution (4%) to which alcohol is ultimately added, and removal of the solvent in a current of carbon dioxide, and, finally, in a vacuum. When exposed to air, the anhydrides dry less rapidly than the corresponding glycerides, but suffer a greater increase in weight owing to hydration to the corresponding acids and oxy-acids. Pure oleic anhydride crystallises in silvery scales, m. p. 22·2°, and can be used for certain culinary operations. Its electrical conductivity in anhydrous acetone is considerably greater than that of oleic acid; glacial acetic acid is not a suitable solvent for this purpose, since it is partly converted into acetic anhydride under the influence of oleic anhydride.

The behaviour of the anhydrides when heated under diminished pressure has been investigated in the case of the compounds from rape-seed oil; under 22 mm. pressure, about 30% distils over and the residue then suddenly becomes transformed into a porous, rubber-like mass probably consisting of polymerised substances which are convertible only with difficulty into the corresponding fatty acids.

Hanus's method is strongly recommended for the estimation of the iodine numbers on account of its accuracy and rapidity. H. W.

Metal Salts of Thioglycollic [α-Thiolacetic] Acid. C. N. MYERS (*J. Lab. Clin. Méd.*, 1921, **6**, 359—373).—α-Thiolacetic acid is prepared by heating chloroacetic acid with potassium hydrogen sulphide, acidifying, and extracting the free acid with ether. When the clear mixture formed by dissolving metallic salts or hydroxides in an aqueous solution of the sodium salt is acidified, acids of the type $SR\cdot CH_2\cdot CO_2H$ are obtained. These are generally crystalline substances readily soluble in water, but decomposing in aqueous solution, especially in light, with the production of a metallic sulphide. Salts of the type $SR\cdot CH_2\cdot CO_2Na$ are obtained by addition of absolute alcohol to solutions of the metallic oxides in sodium α-thiolacetate solution. Compounds of the following were prepared: bismuth, copper, rubidium, silver, gold, glucinum, cadmium, mercury, thallium, cerium, lead, vanadium, arsenic, antimony, molybdenum, tungsten, uranyl, nickel, cobalt, platinum, and zinc. CHEMICAL ABSTRACTS.

The Significance of the Formation of Boro-complexes (and Acetonic Compounds) in Studying the Constitution and Configuration of Polyhydric Alcohols and Hydroxy-acids. J. BÖESEKEN (*Rec. trav. chim.*, 1921, **40**, 553—567).—A summary of work carried out by the author and his students during the past ten years. The following conclusions are drawn: Boric acid in dilute aqueous solution forms strong complex acids with phenols and polyhydric alcohols when the hydroxyl groups are situated

in the same plane and on the same side of the two carbon atoms to which they are attached. The production of these acids is due to the formation of five-, and in some cases six-membered rings. Similar groups exert a repulsive action on each other. The chemical character of the organic portion of the complex has a minor influence on its acidity: the increase in conductivity depends primarily on the favourable position of the hydroxyl groups. The results enable the positions of the hydroxyl groups in space to be determined with respect to each other and to the rest of the molecule with greater certainty than hitherto; theoretical inferences are in accord with the facts when the mobility of molecular structure is taken into account.

The summary deals systematically with each group of organic compounds members of which have been investigated. In solution, the carboxyl group is hydrated to $C(OH)_3$, and in concentrated solution α-keto-carboxylic acids to $-C(OH)_2{\cdot}C(OH)_3$. H. J. E.

The Influence of some α-Keto-acids on the Conductivity of Boric Acid. J. Böeseken and B. B. C. Felix (*Rec. trav. chim.*, 1921, **40**, 568—573).—The increased conductivity of boric acid in presence of pyruvic acid in concentrated solution has been attributed to the hydration of pyruvic acid or, alternatively, to its transformation into an enolic form,

$$CH_3{\cdot}CO{\cdot}CO_2H \longrightarrow CH_2{:}C(OH){\cdot}CO_2H.$$

The latter explanation cannot apply in the case of trimethylpyruvic acid, which gives similar results with boric acid. Three aromatic α-ketonic acids (phenylglyoxylic, mesitylglyoxylic, and phthalonic), each having no hydrogen atom attached to the β-carbon atom, have been examined for comparison. The effect varies in each case to a different amount with the concentration. The conclusion is drawn that, in concentrated solution, hydration of the CO-group, in addition to hydration of the CO_2H-group occurs, dissociation of the former taking place rapidly with dilution.

H. J. E.

The Distinction between α-Hydroxy-acids, $OH{\cdot}CHR{\cdot}CO_2H$ and $OH{\cdot}CRR'{\cdot}CO_2H$, by the Boric Acid Method and the Space Configuration of these Substances. J. Böeseken (*Rec. trav. chim.*, 1921, **40**, 578—581).—As the increase in conductivity in solutions of boric acid caused by the addition of α-hydroxy-acids depends on the space relation of two hydroxyl groups (see above), such increase may be used to distinguish between the two series of acids as for mono-substituted acids, it is less than for di-substituted. The influence of the hydroxyl group increases with the weight of R in the aliphatic series. In the aromatic series, other causes affect the regularity of the increase. When a hydroxyl and a carboxyl group are attached to the same carbon atom which forms part of a ring, the effect seems to decrease. Suggestions are made as to the interpretation of the results with regard to the space configuration of hydrated carboxyl groups.

H. J. E.

The Formation of Oxalic Acid from Lignin. E. Heuser and A. Winsvold (*Cellulosechem.*, 1921, **2**, 113).—Heuser, Roesch, and Gunkel (*Cellulosechem.*, 1921, No. 2) have stated that the alkaline fusion of lignin, prepared by Willstätter and Zechmeister's method, yields little or no oxalic acid. It is now found that a yield of 20% of oxalic acid can be obtained from lignin. Thus, 4 grams of lignin and 50 grams of potassium hydroxide are heated for forty minutes at 280°. The fused mass is dissolved in water, dilute hydrochloric acid added to precipitate unaltered lignin, and from the filtrate, after clarification with animal charcoal in the usual manner, the oxalic acid is precipitated as calcium oxalate (1·016 grams); cf. A., 1919, i, 58, 239, 368. F. M. R.

Preparation of Fumaric Acid. Carl Wehmer (Brit. Pat 146411).—Fumaric acid is obtained by the fermentation of saccharine liquids such as beer wort, grape juice, or solutions of sucrose, dextrose, maltose, etc., containing the requisite nutritive material, with a pure culture of *Aspergillus javanicus*, otherwise known as *A. fumaricus*. For example, 100 grams of sugar in 1 litre of water are sterilised and inoculated with the fungus; 35 grams of calcium carbonate and the usual nutritive salts for the fungus are added, and after two to three weeks' fermentation at 20° about 120 grams of crystalline calcium fumarate will have been deposited from the solution. From this salt fumaric acid is obtained by any of the usual methods. G. F. M.

Experiments on the Synthesis of the Polyacetic Acids of Methane. IV. Conditions of Formation by the Cyanoacetic Ester Method of Stable Methanetriacetic Esters. Christopher Kelk Ingold and Edward Arthur Perren (T., 1921, **119**, 1865—1868).

Experiments on the Synthesis of the Polyacetic Acids of Methane. V. The Preparation of Carboxymethanetriacetic Acid. Christopher Kelk Ingold and Walter James Powell (T., 1921, **119**, 1869—1874).

Phosphoric Esters of some Substituted Glucoses and their Rate of Hydrolysis. P. A. Levene and G. M. Meyer [with I. Weber] (*J. Biol. Chem.*, 1921, **48**, 233—248).—The present paper is a continuation of one by Levene and Yamagawa (A., 1920, i, 712). The rates of hydrolysis of the following phosphoric esters were studied, the amorphous barium salt being employed in each case: (1) ζ-Phosphoric ester of α-, β-, γ-, ε-diacetone-glucose, (2) ζ-phosphoric ester of αβ-monoacetone-glucose, (3) phosphoric ester of αβ-monoacetone-glucose, (4) γ- or ε-phosphoric ester of αβ-monoacetone-glucose, (5) ζ-phosphoric ester of βγε-trimethyl methyl glucoside, (6) β-phosphoric ester of γεζ-trimethyl methyl glucoside. The positions of the phosphoric acid groups, where stated, were determined by the method of preparation. (2), (3), and (4) gave hydrolysis constants of $58(10^{-3})$, $44(10^{-3})$, and $24(10^{-3})$ respectively; the rate of hydrolysis of (1) was identical, and that of (5)

almost identical, with that of (2), whilst (6) did not yield a constant, a result which was attributed to the probable presence of trimethyl glucose as an impurity. The authors conclude from these results that the stability of the phosphoric acid group depends on its position in the sugar molecule. (6) Was prepared by the following method: αβ-monoacetone-glucose was methylated by means of methyl sulphate, giving *γεζ-trimethyl-αβ-monoacetone-glucose*, b. p. 88—90°/0·03 mm., $[\alpha]_D^{20}$ −28·5°. Hydrolysis of this gave γεζ-trimethylglucose, b. p. 147°/0·05 mm., $[\alpha]_D^{20}$ −10·95° initial, −14·6° final, which was converted into *γεζ-trimethylmethylglucoside*, b. p. 135°/0·035 mm., by heating with methyl alcoholic hydrogen chloride (cf. Irvine and Scott, T., 1913, **103**, 573). E. S.

The Constitution of Polysaccharides. III. The Relationship of *l*-Glucosan to *d*-Glucose and to Cellulose. JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM (T., 1921, **119**, 1744—1759).

The Thermal Decomposition of Sucrose under Reduced Pressure. JOSEPH REILLY (*J. Soc. Chem. Ind.*, 1921, **40**, 249—251T).—A study of the dry distillation of sucrose under similar conditions to those which have been employed already with cellulose or starch. On an average, the yield of distillate collected at 60° was about one-quarter that obtained in comparative experiments with cellulose or starch, and was also less than that previously obtained from β-glucose or certain β-glucosides. In the dry distillation of sucrose under reduced pressure, there is much decomposition, and the distillate, after purification, appears to be a mixture which contains substances closely related to the sugars. The presence of *l*-glucosan in the mixture was established through the formation of tribenzoyl-*l*-glucosan, m. p. 198·5—200°, but the amount could represent only a small proportion of the original sucrose molecule. Assuming that the breakdown of sucrose follows similar lines to the breakdown of cellulose under similar conditions, this result indicates the absence of the β-glucose structure as a main grouping in sucrose structure. The presence of a second compound in the distillate was suspected, for a small quantity of a nitrate, white crystals, m. p. 138—145°, was isolated from the products of nitration of the purified distillate and differed from *l*-glucosan trinitrate and lævulosan trinitrate.

The presence of furfuraldehyde in the distillate was shown by the formation of furfuramide, m. p. 117°, furfurylideneacetone, m. p. 39—40°, and the *p*-nitrophenylhydrazone, m. p. 136—137°. Derivatives of furfuraldehyde were also present, but were only qualitatively studied. Acetic acid is the principal acid present in the distillate. During the thermal decomposition of sucrose under reduced pressure, gases and vapour are evolved continuously. In one experiment, formaldehyde was detected, and in other experiments, in which 99 c.c. of gas at 20°/753 mm. were obtained from 1 gram of pure sucrose, the presence of carbon dioxide, carbon monoxide, and unsaturated hydrocarbons, and a saturated hydrocarbon was observed. F. M. R.

Method of Dispersion of Cellulose in Concentrated Aqueous Solutions of Neutral Salts. P. P. von Weimarn (*Kolloid Zeitsch.*, 1921, **29**, 197—198).—An answer to a criticism of Herzog and Beck (this vol., i, 97) of the author's work on the dispersion of cellulose in concentrated aqueous solutions of neutral salts (A., 1912, i, 679). The author points out that whilst cellulose may be dispersed in aqueous solutions of sodium iodide, calcium bromide, calcium iodide, strontium iodide, and barium, calcium, and strontium thiocyanates under atmospheric pressure, in other cases, such as solutions of sodium, potassium, and barium chlorides, increased pressure must be employed. J. F. S.

Swelling and Dispersion of Cellulose in Concentrated Aqueous Solutions. P. P. von Weimarn (*Kolloid Zeitsch.*, 1921, **29**, 198—199).—Cellulose may be dispersed in a solution of any easily soluble salt of a sufficiently great concentration, and the degree of dispersion is so much greater the more soluble and the more hydrated the salt is. Dispersion and swelling of cellulose may also be effected by bringing it into contact with water under a large external pressure. The swelling and dispersion produced by salt solutions increase in the following order: sodium chloride, barium chloride, potassium iodide, strontium chloride, calcium bromide, and lithium chloride at ordinary temperatures and pressures. In the case of sodium chloride, the swelling is scarcely noticeable after the materials have been in contact for five years and eight months, whilst with lithium chloride complete swelling has occurred in a much shorter time. J. F. S.

Chloro-cellulose Esters, and the Action of Chloro-acyl Chlorides on Cellulose. W. Leigh Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 253—256T).—The action of chloroacetyl chloride and also of the mixed chloroacetic-acetic anhydride on cellulose is one of esterification accompanied by resolution of the cellulose coupled with partial hydration of the cellulosic residue. The hydration occurs during the treatment of the ester with water while it is being freed from acidic impurities. More than fifty preparations were made from cellulose and chloroacetyl chloride under different conditions, and in many cases the reaction could not be checked in time to isolate solid esters insoluble in water, for, in general, rapid degradation of the complex accompanied esterification, and resulted in the formation of water-soluble esterified carbohydrates. In a typical preparation, 1 gram of cellulose was moistened with acetic acid (which just previously had been coloured by chlorine) and the excess liquid removed by squeezing; 10 c.c. of a mixture of 1 part of pyridine with 2 parts of toluene were added; and then slowly with stirring 8 c.c. of chloroacetyl chloride, containing a trace of sulphur dioxide. The cellulose gelatinised gradually, and the solution became very dark, but cleared somewhat on warming. The gelatinous mass obtained on cooling consisted of a product soluble in alcohol, cellobiose heptaacetate, and a *cellulose glycollate*, $[C_6H_7O_2(CO_2 \cdot CH_2 \cdot OH)_3]_7,HCl$, soluble in ether, finally obtained as a white powder, m. p. 237—238°.

The glycollic esters of cellulose were investigated further, and a large number of mixed esters, with definite melting points and great solubility in acetone, were obtained, for example,

$$[(C_6H_7O_2)_3(CO_2\cdot CH_2\cdot OH)_7(OAc)_2]_{12},10HCl,$$

a white powder, m. p. 256°. The action of dichloroacetyl chloride on cellulose in presence of pyridine, diluted with benzene, is more vigorous; the products are not uniform, but consist of cellulose acetates with chlorinated esters. The esterification of cellulose proceeds smoothly with chloroacetyl chloride in acetic acid solution together with traces of chlorine and sulphur dioxide, and the products can be isolated as required. The products all correspond with the general formula $(C_{14}H_{20}O_{10})_nHCl$, and appear to be mixed esters of acetic and hydracrylic acids. They are powders possessing definite melting points which decrease with diminution in the value of n, whilst the chlorine content increases. When melted they form transparent liquids which solidify to almost colourless resins on cooling. For example, $(C_{14}H_{20}O_{10})_{12}HCl$, m. p. 225—226°; $[C_6H_7O_2(CO_2\cdot CH_2\cdot CH_2\cdot OH)_2\cdot OAc]_{18},HCl$, m. p. 222°, which forms a red *p-bromophenylhydrazone*, m. p. 196° with decomp.; $(C_{14}H_{20}O_{10})_{11}HCl$, m. p. 202°; $(C_{14}H_{20}O_{10})_{13}HCl$, m. p. 224—225°, which forms a *benzoate*, m. p. 230°; $(C_{14}H_{20}O_{10})_8HCl$, softens at 190°, m. p. 202°; $(C_{14}H_{20}O_{10})_4HCl$, with no definite melting point, but forms a syrup at 168°.

Attempts to prepare a similar series of products by using mixed acetic-chloroacetic anhydride, $CH_3\cdot CO\cdot O\cdot CO\cdot CH_2Cl$, led to products of the general formula $[C_6H_7O_2(OAc)_3]_n,HCl$.

At no stage in any of the series of cellulose esters, or derivatives therefrom, is there an abrupt change in properties, but throughout as the magnitude of the cellulose complex diminishes so the physical constants such as solubility and melting point become clearly defined, and also follow a general order, the solubilities increasing and the melting points decreasing with diminution of the number of cellulose units left in the esters. F. M. R.

Investigation of the Viscosity of Cellulose Acetates. ANNA VON FISCHER (*Kolloid Zeitsch.*, 1921, **29**, 260—265).—It is shown that the suitability of a cellulose acetate for the production of a plastic substance cannot be decided from its viscosity alone, but from the viscosity–composition curve. The viscosity of cellulose acetate in a series of solvents has been investigated, and the influence of temperature determined in some cases. The solvents examined were: acetone, acetone–alcohol, acetone–20% camphor, acetone–40% camphor, acetone–10% triacetin, acetone–25% dichlorohydrin, acetone–50% dichlorohydrin, and acetone–10% *p*-toluenesulphonamide. It is shown that the thirty-nine specimens of cellulose-acetate examined may be classed in seven viscosity types. A viscosity minimum in a mixture of acetone and alcohol containing 90 vol. % of acetone indicates an unusable cellulose acetate; whilst a cellulose acetate which gives a minimum viscosity in the mixed solvent containing 80 vol. % of acetone is a particularly usable specimen. Between the good type, 7, and the poor type, 1, no

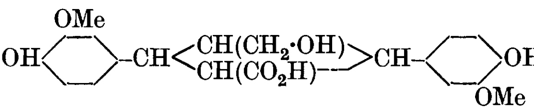
difference could be found in the viscosity curves. Addition of Japanese camphor and triacetin increases the viscosity of cellulose acetate in pure acetone solution. The addition of dichlorohydrin and *p*-toluenesulphonamide increases the viscosity of solutions of the one cellulose acetate but decreases that of the other. Preliminary experiments on the viscosity of solutions of cellulose nitrate are described. J. F. S.

Relation to Lignin of Crude Resin and Tannic Acid in Spruce Needles. A. C. VON EULER (*Svensk. Pappers-Tid.*, 1921, **24**, 191—195).—A summary and extension of conclusions based on investigations by Klason (A., 1920, i, 148, 474, 821).
CHEMICAL ABSTRACTS.

Lignin Substance. K. H. A. MELANDER (*Svensk. Pappers-Tid.*, 1921, **24**, 195—196).—Review of a dissertation by I. L. Hochfelder. By digestion of spruce chips with phenol, two substances, "lignin substance-α" (insoluble in ethyl ether) and "lignin substance-β" (soluble in ethyl ether) were obtained in the proportions of 23·1% and 18·6% respectively. The molecule of the former contains three hydroxyl groups, but no carboxyl or carbonyl groups. CHEMICAL ABSTRACTS.

Lignin. I. Sulphite Liquor Lactone. BROR HOLMBERG (*Ber.*, 1921, **54**, [*B*], 2389—2406).—Much of this paper has been already published (this vol., i, 25).

If, as proposed, the sulphite liquor lactone is that of diguaiacyltetramethylenecarbinolcarboxylic acid, the latter will have the constitution,



or

$OH\cdot CH_2\cdot CH\cdot CH\cdot C_6H_3(OH)\cdot OMe$
$CO_2H\cdot CH\cdot CH\cdot C_6H_3(OH)\cdot OMe.$

The lactone crystallises in small, white, six- or eight-sided plates or in flat, oblique, or wedge-shaped or triangular, pointed prisms, and in boiling acetone has the molecular weight corresponding with the formula $C_{20}H_{20}O_6$. In alcoholic solution, it gives with ferric chloride a green coloration changing to brown, and with nitrite and concentrated sulphuric acid a brown solution, becoming green and then violet. With phloroglucinol and hydrochloric acid, it gives no reaction, but an alkaline solution which has been attacked by the air gives an intense cherry-red coloration with this reagent; the lignosulphonic acids of sulphite liquors exhibit similar behaviour (cf. Klason, A., 1918, i, 59).

The corresponding hydroxy-acid separates in bundles of capillary or fine, acicular crystals; various salts are described. The amide has $[\alpha]_D^{20}$ +85°, and the diacetyl derivative of the lactone $[\alpha]_D^{20}$ −73·5°.

Sulphonation of the lactone and subsequent treatment with water yields a *monosulphonic acid* of the hydroxy-acid, $C_{20}H_{22}O_{10}S$,

which forms a crystalline powder, m. p. 172—173° (decomp.); the *barium* salt of this acid was analysed.

When brominated in ethereal solution at the ordinary temperature, the lactone yields: (1) a *tribromo*-derivative, $C_{20}H_{17}O_6Br_3$, which crystallises in small, acicular prisms united to stellar or leaf-like aggregates, sintering at about 230°, m. p. 238—240° (decomp.), $[\alpha]_D^{22}$ +20·5°, and (2) a *tetrabromo*-derivative, $C_{20}H_{16}O_6Br_4$, forming small, brownish-yellow crystals, sintering and darkening at about 255°, m. p. 260° (decomp.), $[\alpha]_D^{23}$ +30·9°.

When oxidised by means of various reagents, the lactone or the hydroxy-acid gives no definite compounds other than oxalic acid. The lactone withstands virtually without alteration a temperature of 220—230°, but at 250—260°, either at the ordinary, or slightly reduced, pressure, it undergoes transformation into products apparently identical with those obtained by treating the lactone either in the cold or more rapidly in the hot with sodium ethoxide. One such product, m. p. 210—211°, $[\alpha]_D^{20}$ +28°, contained 64·8% C and 5·9—6·1% H, and another, m. p. 210—212°, $[\alpha]_D^{20}$ +29°, 65·5—66·0% C, and 6·1—5·9% H; others showed the same melting points and rotatory powers as these, but varied in composition between that of the lactone and that of the acid. T. H. P.

Lignin. II. Dimethyl-sulphite-liquor Lactone. BROR HOLMBERG and MARTIN SJÖBERG (*Ber.*, 1921, **54**, [*B*], 2406—2417).—Treatment of the lactone previously described (preceding abstract) with methyl sulphate yields its dimethyl derivative, to which the name α-dimethyl-sulphite-liquor lactone is given. This lactone, when subjected to the action of sodium ethoxide, is converted into the optically inactive β-dimethyl-sulphite-liquor lactone, which is not a racemic compound but is apparently diastereomeric with the α-compound, and may be hydrolysed to an optically active, stereochemically individual hydroxy-acid.

That portion of the ethereal extract of the sulphite liquors which is soluble in alcohol is found to contain small proportions of pyromucic and vanillic acids.

The *α-dimethyl-lactone*, $C_{18}H_{12}O_2(OMe)_4$, forms white, silky, capillary crystals, m. p. 179—180°, $[\alpha]_D^{18}$ −100·9°, $[\alpha]_D^{20}$ −99·2°, and, when heated in a vacuum, yields white, crystalline sublimates and a residue consisting largely of the β-compound. The corresponding *hydroxy-acid*, $C_{22}H_{26}O_7$, forms slender capillary crystals, m. p. 150—156° (frothing), $[\alpha]_D^{19}$ +38·5°, $[\alpha]_D^{20}$ +38·9°; various salts are described. Oxidation of the lactone in different ways yields principally oxalic acid.

The *β-dimethyl-lactone*, $C_{22}H_{24}O_6$, separates in flat, white needles or capillary crystals, m. p. 142—143°. The *β-dimethyl-hydroxy-acid*, $C_{22}H_{26}O_7$, crystallises in superimposed, colourless, rectangular plates (+$3\frac{1}{2}H_2O$), m. p. about 95° (not sharp), $[\alpha]_D^{20}$ +52·1 to 52·6°. T. H. P.

Lignin. III. Alkali Lignins. BROR HOLMBERG and TEODOR WINTZELL (*Ber.*, 1921, **54**, [*B*], 2417—2425).—The authors have

investigated the so-called black liquor obtained as waste product in the soda-cellulose process; the original wood was mainly pine, 1 part of sodium oxide being used in the extraction of 5·8 parts of absolutely dry wood, and no sodium sulphide being employed. With this liquor, sulphuric, hydrochloric, acetic, and carbonic acids gave apparently identical precipitates, which are separable by treatment with alcohol into two principal fractions: (1) α-Lignin, which is insoluble in alcohol, has a composition corresponding with the empirical formula, $C_{40}H_{42}O_{13}$, and (2) λ-lignin, soluble in alcohol and having a composition corresponding with $C_{40}H_{44}O_{12}$. Both are greyish-yellow to yellowish-brown, amorphous powders, and both readily yield colloidal solutions and behave like phenolic compounds of high molecular weight. Each contains between three and four methoxyl groups per C_{40}-complex, this number being increased to about six by treatment of the lignin with methyl sulphate. When fused with potassium hydroxide, as described by Hönig and Fuchs (A., 1920, i, 291), these lignins yield, like the ligninsulphonic acids of sulphite liquors (Melander, A., 1919, i, 473), acetic and protocatechuic acids, and also oxalic acid. Attempts to obtain definite degradation products by oxidising the lignins or by heating at low pressures have as yet been unsuccessful. T. H. P.

Dimethylvinylamine. KURT H. MEYER and HEINRICH HOPFF (*Ber.*, 1921, **54**, [*B*], 2274—2282; 2942).—Dimethylvinylamine, $NMe_2\cdot CH\!:\!CH_2$, has been prepared in moderate yield by the dry distillation of neurine chloride. It fulfils the theoretical expectations of Meyer and Lenhardt (A., 1913, i, 723) and Meyer (this vol., i, 855) in that it is an exceedingly reactive product which is particularly characterised by the great readiness with which it undergoes polymerisation.

Dimethylvinylamine, a mobile liquid, b. p. 37—38°, is obtained by the dry distillation of neurine chloride, the operation being interrupted when the thermometer (in the vapour) records 80°. It readily unites with bromine in cold hydrochloric acid solution and couples with diazotised nitroaniline in acetic acid solution to an unstable orange azo-dye. It is decomposed into dimethylamine and acetaldehyde by warm dilute hydrochloric acid. The freshly-distilled base becomes completely polymerised to a white solid within twelve hours.

Neurine is prepared by the action of freshly-precipitated silver oxide on a concentrated aqueous solution of trimethyl-β-bromoethylammonium bromide and isolated as the colourless, crystalline *trihydrate* by concentration of the filtered solution in a high vacuum over phosphoric oxide at 5—10°; it is extremely hygroscopic and decomposes with great readiness when its solution is slightly warmed. When subjected to dry distillation, neurine gives a small amount of dimethylvinylamine, but is mainly decomposed into trimethylamine and vinyl alcohol, which is isolated as acetaldehyde.

Choline has been isolated as a colourless, extremely hygroscopic,

crystalline substance which, when distilled, decomposes in all three possible directions, yielding mainly trimethylamine and ethylene glycol, with smaller amounts of β-dimethylaminoethyl alcohol and minimal quantities of dimethylvinylamine. Under similar conditions, choline chloride gives β-dimethylaminoethyl alcohol and methyl chloride.

Attempts to prepare diethylvinylamine by the following sequence of reactions are described. β-Diethylaminoethyl alcohol is transformed by hydrobromic acid (66%) at 130—135° into *α-bromo-β-diethylaminoethane hydrobromide*, $NEt_2{\cdot}CH_2{\cdot}CH_2Br,HBr$, colourless needles, m. p. 209°, from which α-bromo-β-diethylaminoethane is obtained as a colourless liquid which readily undergoes polymerisation, b. p. 63°/0·3 mm. (In alcoholic solution it is speedily transformed into *tetraethylpiperazonium dibromide*,

$$\begin{matrix}Br\\Et_2\end{matrix}{>}N{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}N{<}\begin{matrix}Et_2\\Br\end{matrix},$$

colourless platelets or short prisms, decomp. 308°.) The action of a very large excess of pure liquid trimethylamine on freshly-distilled α-bromo-β-diethylaminoethane leads to the formation of *β-diethylaminoethyltrimethylammonium bromide*,

$$NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br,$$

colourless, hygroscopic crystals, m. p. 208°, which is transformed by silver oxide into the corresponding crystalline ammonium *base*. The latter is decomposed when distilled giving minute amounts of *diethylvinylamine*, water, and trimethylamine and mainly methyl alcohol and *α-dimethylamino-β-diethylaminoethane*, a colourless liquid with a faint odour of ammonia, b. p. 156—157° (the *dihydrobromide*, m. p. 207—208°, *platinichloride*, yellow octahedra, m. p. 220°, and *picrate*, lemon-yellow needles, m. p. 240°, are described). α-Bromo-β-diethylaminomethane gives small quantities of diethylvinylamine when distilled with powdered potassium hydroxide. H. W.

Manufacture of Additive and Condensation Products containing Nitrogen from Acetylene and Ammonia. CHEMISCHE FABRIK RHENANIA AKT.-GES., BERNHARD CONRAD STUER, and WALTHER GROB (Brit. Pat. 147067).—Condensation products of acetylene and ammonia are obtained by passing the mixed gases in either a dry or moist condition, at normal or increased pressures, over catalysts, other than metals or metallic nitrides, such as, particularly, the oxides of iron or natural ores of iron, such as bog ore, bauxite, or chrome ironstone. The temperature of the reaction may vary within wide limits; the higher the temperature, the further the condensation proceeds. For example, at about 350° the reaction $C_2H_2+NH_3=CH_3{\cdot}CN+H_2$ predominates. Further condensation between 2 or 3 mols. of acetylene and 1 mol. of ammonia results in the formation of pyrrole and picoline respectively, and at 550° the formation of the latter substances and their homologues becomes more pronounced. For obtaining acetonitrile, the gases escaping from the contact space are cooled and the condensate is distilled, aqueous acetonitrile passing over at 72—80° G. F. M.

The Valency Problem of Sulphur. V. Molecular Weight of Thiocyanogen. HANS LECHER and ALFRED GOEBEL (*Ber.*, 1921, **54**, [*B*], 2223—2229; cf. this vol., i, 414).—The instability of isolated thiocyanogen (Söderbäck, A., 1920, i, 219) renders the estimation of its molecular weight in solution a matter of difficulty. This, however, can be accomplished by the cryoscopic method by allowing a known weight of bromine to react with lead thiocyanate in the presence of bromoform, $Pb(SCN)_2+Br_2=PbBr_2+(SCN)_2$, and measuring the depression of the freezing point thus caused. Perfectly colourless solutions are obtained which cannot contain more than traces of free bromine. Preliminary experiments show that lead bromide and thiocyanate are practically insoluble in bromoform, that the former does not combine with bromine to yield a tetrabromide, and that the latter does not unite with thiocyanogen to give a tetrathiocyanate under the experimental conditions adopted. The molecular formula of bromine in freezing bromoform is Br_2. Even in very dilute solution, thiocyanogen shows no sign of dissociation, the molecular weight in 0·026—0·278*N* solution remaining constant and in good agreement with that required by the formula $(CNS)_2$. In more concentrated solution (0·548—1·095-*N*), a reversible association is observed to some extent, which is shown conclusively not to be due to incipient decomposition and consequent formation of polymerised products. It follows, therefore, that free thiocyanogen shows no analogy with the hexa-arylethanes, as suggested by Söderbäck (*loc. cit.*). The great reactivity of the substance is probably to be ascribed to the affinity of the sulphur atoms towards electrons; the substance thus falls into line with the halogens in this respect (cf. Born, A., 1919, ii, 214; 1920, ii, 156; Fajans, A., 1920, ii, 12).

H. W.

The Friedel-Crafts' Reaction. III. Migration of Alkyl Groups in the Benzene Nucleus. MAURICE COPISAROW [with CYRIL NORMAN HUGH LONG] (T., 1921, **119**, 1806—1810).

Manufacture of Chlorinated Derivatives of Toluene. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and DOUGLAS ARTHUR CLIBBENS (Brit. Pat. 169025).—The chlorination in aqueous solution of toluene-*p*-sulphonic acid or its soluble salts results in the formation of 2 : 5-dichloro- and 2 : 5 : 6-trichloro-toluene-4-sulphonic acids, which are readily separated from one another by taking advantage of the much greater insolubility in water of the sodium salt of the trichloro-acid. If 680 grams of toluene-*p*-sulphonic acid neutralised with sodium hydroxide and dissolved in sufficient water to make about 11 litres are chlorinated until 10 c.c. of the solution have acquired an acidity equivalent to 5·5 c.c. of *N*-alkali, nearly the whole of the sodium 2 : 5 : 6-trichlorotoluene-4-sulphonate separates out in crystals, and the dichlorosulphonate is recovered in a practically pure condition by evaporating the mother-liquor. The sulphonates on hydrolysis give good yields of pure 2 : 5-dichloro- and 2 : 5 : 6-trichloro-toluene respectively.

G. F. M.

Manufacture of Chlorinated Derivatives of Toluene. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and ALFRED EDWIN HERBERT (Brit. Pat. 170056).—The chlorination of toluene-*o*-sulphonic acid or its soluble salts in cold aqueous solution results in the formation of a mixture of the 4-chloro- and 6-chloro-derivatives, which are readily separated owing to the much greater solubility of the salts of the 4-chloro-acid. Thus if a suitable concentration is selected, pure sodium 6-chlorotoluene-*o*-sulphonate separates and the mother-liquor on evaporation yields almost pure sodium 4-chlorotoluene-*o*-sulphonate, from which salts, by hydrolysis, pure 4-chloro- and 6-chloro-toluene are obtainable. By chlorinating in more dilute solution at a temperature not exceeding 60°, a mixture of dichloro- and trichloro-toluene-*o*-sulphonic acids is produced, from which the latter can easily be isolated on account of the sparing solubility in water of their sodium salts. G. F. M.

Pentabromobenzene. ALFRED ECKERT (*J. pr. Chem.*, 1921, [ii], **102**, 362).—The compound, m. p. 293°, previously regarded as pure pentabromobenzene (A., 1915, i, 566), is found to be contaminated with hexabromobenzene, which is formed by the action of concentrated sulphuric acid on the pentabromo-compound. When pure, the latter has m. p. 159—160° (cf. Jacobsen and Loeb, A., 1900, i, 281). T. H. P.

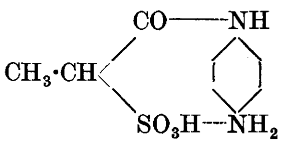
***o*-Chlorodinitrotoluenes. IV. 2-Chloro-3 : 4-dinitrotoluene.** GILBERT T. MORGAN and THOMAS GLOVER (T., 1921, **119**, 1700—1706).

***mm'*-Dinitrodiphenylsulphone.** J. MARTINET and A. HAEHL (*Compt. rend.*, 1921, **173**, 775—777).—The dinitrodiphenylsulphone obtained by Gericke (*Annalen*, 1856, **100**, 211) by the direct nitration of diphenylsulphone, and considered by him to be the *oo'*-, is now shown to be the *mm'*-compound. On reduction with tin and hydrochloric acid, it gives *mm'*-diaminodiphenylsulphone, m. p. 168° (cf. Gericke, *loc. cit.*), which yields a *nitrate*, a *picrate*, an *oxalate*, m. p. 175°, and a *diacetyl* derivative. When the diamine is diazotised and the subsequent solution added to boiling dilute sulphuric acid, dihydroxydiphenylsulphone, m. p. 186—187°, previously prepared by Tassinari from *p*-bromophenol (cf. A., 1887, 807; 1889, 245), is obtained. W. G.

Production of Alkylanilines. E. I. DU PONT DE NEMOURS and Co. (Brit. Pat. 145743).—Alkylanilines are obtained by heating together at a high temperature aniline, an alcohol, and a catalyst containing iodine, such as methyl iodide, hydrogen iodide, or ammonium iodide. For example, 96 parts of methyl alcohol, 93 parts of aniline, and 1·35 parts of methyl iodide may be heated in a digester at 220—240°. The liquids separate into two layers, one containing dimethylaniline, and the other the excess of alcohol used, water, and solid iodine compounds, which are recovered by distilling off the alcohol and evaporating to dryness. The residue

is likewise catalytically active, and may be employed in subsequent operations instead of methyl iodide. G. F. M.

The Action of α-Sulphopropionic Acid on some Aromatic Mono- and Di-amines. H. J. BACKER (*Rec. trav. chim.*, 1921, **40**, 582—592).—The action of α-sulphopropionic acid on excess of an amine is in the first place to produce a compound by condensation of the carboxyl group of the acid with the NH_2-group, and, secondly, for the sulphonic group to react with a second molecule of the amine. The second amine molecule may be replaced by an inorganic base, and by preparing barium salts in this manner the arylaminepropion-α-sulphonic acids may be obtained by the action of sulphuric acid. In the case of β-naphthylamine, the second molecule of the amine reacts to form a molecule of β-dinaphthylamine. Some diamines react in such a way that the second NH_2-group fulfils the same function as the second molecule of a primary amine, thus *p*-phenylenediamine forms a compound to which the annexed formula is attributed.



The following compounds have been prepared: α-*Sulphopropionanilide*, SO_3H·CHMe·CO·NHPh, a white, hygroscopic substance, m. p. about 205°, its *aniline* ester, white needles, m. p. about 255°, its *sodium, barium, copper, copper ammonium, copper pyridine*, and *cobalt* salts; the p-*toluidine* ester of α-*sulphopropion*-p-*toluidide*, white needles, m. p. about 251°, also the *sodium* salt; p-*anisidine* α-*sulphopropionate*, violet powder, m. p. 122°, its p-*anisidide*, bluish-violet crystals, m. p. 242°. p-*Phenetidine* α-*sulphopropionate*, m. p. 148°, the corresponding p-*phenetidide*, violet plates, m. p. 252°. β-*Naphthylamine* α-*sulphopropionate*, white substance, m. p. 203°. p-*Phenylenediamine* α-*sulphopropionate*, violet, crystalline powder, m. p. 210° (decomp.). α-*Sulphopropion*-p-*aminoanilide*, dark blue powder, m. p. 240° (decomp.). o-*Phenylenediamine* α-*sulphopropionate*, brown powder, m. p. 165°. *Benziminazole-2-ethyl-α-sulphonic acid*, $C_7N_2H_5$·CHMe·SO_3H, a grey, crystalline powder, *benziminazole-2-sulphonic acid*, small, white needles, m. p. above 300°. The formation of the last two substances, by the action of α-sulphopropionic acid on *o*-phenylenediamine, provides a simple method for the preparation of iminazole and its derivatives. H. J. E.

Substitution Processes. KURT H. MEYER (*Ber.*, 1921, **54**, [*B*], 2265—2273).—The remarkable reactivity of phenol in contrast with benzene has been explained by supposing it to react in the ketonic form and also by the assumption that the hydroxyl group enables it to form primary ether-like additive compounds which only pass secondarily into nuclear-substituted products. Neither theory is, however, tenable, since it is found (cf. Meyer and Lenhardt, A., 1913, i, 723) that phenolic ethers are as reactive as the phenols themselves. It appears to be a perfectly general rule that all double bonds (aliphatic, aromatic, or heterocyclic, simple or conjugated, C:C or C:N·) have increased capacity for reaction

in the presence of hydroxyl-, methoxyl-, amino-, or dimethyl-amino-groups and become "activated" towards diazo-compounds, nitrous acid, oxidising agents, halogen, etc. Phenol is therefore simply a member of a large class of products with "active double bond."

The parallelism between aliphatic and aromatic compounds is shown in the increasing reactivity in the series, ethylene, vinyl ethyl ether, dimethylaminovinylamine (Meyer and Hopff, this vol., i, 851), on the one hand, and benzene, anisole, and dimethyl-aniline, on the other.

According to the author's conception, substitution in phenols, enols, etc., is a reaction of the double bond, probably dependent on primary addition; the hydroxyl- and similar groups only play the part of activators and make the double bond more highly reactive. Evidence in favour of this view is found in the ability of aliphatic hydrocarbons to couple with diazo-compounds (Meyer and Schoeller, A., 1920, i, 97) and the extension of this reaction to aromatic hydrocarbons, for example, mesitylene (Meyer and Tochtermann, this vol., i, 895). The close connexion between ortho- and para-substitution is thus simply a case of 1 : 2- and 1 : 4-addition such as is observed frequently with aliphatic conjugated double bonds.

The hypotheses that mesitylene, aniline, and phenol show in principal similar substitution reactions leads to the conclusion that the primary action is also additive in the cases of the latter compounds. An apparent difficulty therefore arises in the interpretation of the observations that many amines, particularly aniline, and many phenols react with diazonium salts to yield compounds in which the diazo-residue is attached to the nitrogen or oxygen atom. This difficulty is removed if, for example, diazoaminobenzene is not regarded as a necessary intermediate product in the preparation of aminoazobenzene. Evidence is adduced to show that the latter is not formed by the transformation of diazoaminobenzene, but either by the action of the latter or of re-formed diazonium chloride on aniline. Incidentally, the formation of diazoamino-compounds in the coupling process can be completely avoided and the operation can be conducted in such a manner as to lead directly to aminoazo-products.

The groups can be arranged in order of their increasing activation of the degree of unsaturation as follows: ·Me, ·OMe, ·OH, $\cdot NH_2$, $\cdot NMe_2$. Measurements of the rate of hydrolysis of aromatic bromo-compounds by alcoholic sodium hydroxide solution at 180° shows, as is to be expected, that the exaltation of additive capacity is paralleled by increase in the firmness of the anion of the bromine atom in the benzene ring (the experimental material comprises bromobenzene, *p*-bromotoluene, *p*-bromoanisole, *p*-bromophenol, *p*-bromoaniline, *p*-bromodimethylaniline). Conversely, the presence of groups which diminish the additive capacity, for example, NO_2, increase the reactivity of the halogen atoms. Further, in the case of the tetra-arylhydrazines, it is to be expected that increase in the unsaturated nature of the benzene ring would increase the

dissociability; this is found to be the case, the effect of the various groups being exactly similar to that which they exert on the reactive capacity of the double bonds.

All activating groups which are attached to the terminal carbon atom of a conjugated system cause exaltation of the molecular refraction, the extent of which is exactly parallel to the chemical influence of the groups.

[With HEINRICH HOPFF and WALTER FELIX.]—*p*-Nitro-*p'*-aminoazobenzene, m. p. 137°, is formed by the addition of solid aniline hydrochloride to a solution of sodium nitrosoamine and hydrochloric acid in water. *p*-Aminoazobenzene is prepared directly by the treatment of a solution of benzenediazonium chloride in water with a concentrated aqueous solution of aniline hydrochloride. Diazoaminobenzene is converted by *m*-toluidine at 35° in the presence of a little *m*-toluidine hydrochloride into benzeneazo-*m*-toluidine, m. p. 76°. H. W.

Freezing-point Curve of *o*-Cresol–Naphthalene. F. H. RHODES and F. E. HANCE (*J. Physical Chem.*, 1921, **25**, 491—494).—The freezing-point curve of the system *o*-cresol–naphthalene has been determined, and it is found that the eutectic point lies at 20·6° and the eutectic mixture contains 22·5% of naphthalene. The system is remarkable on account of the ease with which mixtures containing relatively large amounts of *o*-cresol are supercooled. So much so is this that mixtures containing far more *o*-cresol than the eutectic percentage on seeding with a crystal of naphthalene will deposit naphthalene. Such mixtures often show two "freezing points," one at which solid *o*-cresol is in stable equilibrium with the mother-liquor and a second and lower one at which solid naphthalene is in metastable equilibrium with a supercooled cresol-rich mother-liquor. J. F. S.

Geometrical Isomerism of *iso*Safrole. SHŌICHIRŌ NAGAI (*J. Coll. Eng. Tokyo*, 1921, **11**, 83—100).—By gentle isomerisation of safrole with a small quantity of dilute alcoholic potassium hydroxide at 82—86°, a new unstable form of *iso*safrole was obtained, which was easily transformed into the stable form under the influence of a higher temperature and more concentrated potassium hydroxide solution. The new substance, which is shown to be a geometrical isomeride of the stable *iso*safrole, boils at 242—243°, *d* 1·1162—1·1168, and μ=1·5630, all of which figures are lower, as is usual with a *cis*-isomeride, than the constants of the stable form, namely, b. p. 247—248°, *d*=1·1230, and μ=1·5730. The two picrates also showed a difference in m. p. in the same way, namely, 68·5° and 73·5° respectively. Transformation of the *trans*- into the *cis*-form and vice versa was effected through the corresponding dibromo-additive products, which, on distillation in a vacuum, were converted into monobromo*iso*safroles with loss of a molecule of hydrogen bromide. The *trans*-form gives, of course, a *cis*-monobromo-compound and vice versa, and the latter on reduction with zinc dust and ethyl alcohol were reconverted into *iso*safroles, thus completing the cycle. Confirmation of the provisionally assigned

structure of the two *iso*safroles was obtained in the different behaviour of the monobromo*iso*safroles towards alcoholic potassium hydroxide. The above designated *cis*-monobromo-compound readily lost a further mol. of hydrogen bromide with the formation of piperonylallylene, whereas the monobromo-compound derived from the unstable *cis*-*iso*safrole required a much higher temperature and a large excess of potassium hydroxide. Oxidation of both *cis*- and *trans*-*iso*safrole with potassium dichromate or with ozone gave practically identical yields of piperonal from either isomeride, namely, about 35% with dichromate, and 67—69% with ozone. *cis*- and *trans*-*iso*Safrole dibromides were prepared by bromination in carbon disulphide solution. They were identical in properties except in optical rotation, and became turbid on keeping owing to the liberation of hydrogen bromide. For the *cis*-dibromide $[\alpha]_D^{20}$ +13·35, and for the *trans*-compound $[\alpha]_D^{20}$ +4·45. trans-*Bromo*iso*safrole* has *d* 1·442, μ_D^{15} 1·555, b. p. 155—156°/20 mm., and does not become turbid on keeping. cis-*Bromo*iso*safrole* has *d* 1·4532, μ_D^{15} 1·598, and b. p. 169—170°/19 mm. Like the dibromides, it becomes turbid on keeping, and with alcoholic potassium hydroxide at 70°, it is converted into *piperonylallylene*, white crystals, m. p. 41—42°, b. p. 249—251°, having a fragrant odour, and giving an intense violet coloration with sulphuric acid, and red with nitric acid. G. F. M.

Aromatic Nitro-derivatives. XV. Substitution in the Benzene Nucleus. MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1921, **51**, ii, 169—173; cf. this vol., i, 556).—The authors have investigated the behaviour of 2 : 4 : 5-trinitrotoluene towards the three aminophenols and the three aminobenzoic acids. In each case one nitro-group of the trinitrotoluene is eliminated as nitrous acid, a diphenylamine derivative being formed. The action of β-(2 : 3 : 4-) trinitrotoluene on *o*-aminophenol and on *p*-aminoacetophenone has also been studied.

4′ : 6′-*Dinitro-2-hydroxyphenyl*-m-*tolylamine*,

$$C_6H_2Me(NO_2)_2\cdot NH\cdot C_6H_4\cdot OH,$$

obtained from 2 : 4 : 5-trinitrotoluene and *o*-aminophenol, crystallises in lustrous, red or yellowish-brown lamellæ, m. p. 202—203°, and dissolves in alcohol to a deep red solution, and in sulphuric acid to a solution which gradually turns blue. Its *acetyl* derivative, $C_{15}H_{13}O_6N_3$, forms lustrous, yellow needles, m. p. 132°, and dissolves in sulphuric acid, giving a deep blue solution.

4′ : 6′-*Dinitro-3-hydroxyphenyl*-m-*tolylamine*, $C_{13}H_{11}O_5N_3$, from 2 : 4 : 5-trinitrotoluene and *m*-aminophenol, forms garnet-red, prismatic crystals, m. p. 197—198°, gives a violet solution in concentrated sulphuric acid and an alcoholic solution turned deep red by addition of alkali. The *acetyl* derivative, yellow needles, m. p. 122°, forms a violet coloration with concentrated sulphuric acid.

4′ : 6′-Dinitro-4-hydroxyphenyl-*m*-tolylamine, from 2 : 4 : 5-trinitrotoluene and *p*-aminophenol, was obtained by Reverdin and Crépieux (A., 1900, i, 638), and its acetyl derivative by Reverdin, Dresel, and Delétra (A., 1904, i, 580).

2′ : 6′-*Dinitro-2-hydroxyphenyl-*m-*tolylamine*, $C_{13}H_{11}O_5N_3$, obtained from 2 : 3 : 4-trinitrotoluene and *o*-aminophenol, forms garnet-red prisms, m. p. 144—145°, and dissolves in concentrated sulphuric acid to a violet-red solution.

o-4′ : 6′-*Dinitro-*m-*toluidinobenzoic acid*,

$$C_6H_2Me(NO_2)_2\cdot NH\cdot C_6H_4\cdot CO_2H,$$

from 2 : 4 : 5-trinitrotoluene and anthranilic acid, crystallises in reddish-yellow needles, m. p. 244—245°, gives a pale yellow solution in sulphuric acid, and yields an alcoholic solution coloured reddish-brown by alkali.

m-4′ : 6′-*Dinitro-*m-*toluidinobenzoic acid*, $C_{14}H_{11}O_6N_3$, from 2 : 4 : 5-trinitrotoluene and *m*-aminobenzoic acid, forms yellow prisms, m. p. 247—248°, and gives a reddish-brown coloration with alkalis.

p-4′ : 6′-*Dinitro-*m-*toluidinobenzoic acid*, $C_{14}H_{11}O_6N_3$, crystallises in orange-yellow needles, m. p. 269—270°, and gives a pale yellow coloration with concentrated sulphuric acid.

p-2′ : 6′-*Dinitro-*m-*toluidino-acetophenone*,

$$C_6H_2Me(NO_2)_2\cdot NH\cdot C_6H_4Ac,$$

prepared from 2 : 3 : 4-trinitrotoluene and *p*-aminoacetophenone, forms lustrous, garnet-red prisms, m. p. 178°, gives a red solution with concentrated sulphuric acid, and yields deep reddish-brown salts with alkalis. T. H. P.

Sulphoacetic Acid as Condensing Agent. II. Synthesis of Tri-*p*-anisylbenzene from Anisole. WILHELM SCHNEIDER and FRITZ SEEBACH (*Ber.*, 1921, **54**, [*B*], 2298—2302; cf. Schneider and Meyer, this vol., i, 680).—The course of the reaction between anisole and acetic anhydride in the presence of sulphoacetic acid depends greatly on the relative proportions of sulphuric acid and acetic anhydride used in preparing the latter (cf. Schneider and Seebach, this vol., i, 878). With a mixture similar to that used in preparing diphenylmethylpyrylium compounds from acetophenone, anisole does not give a trace of di-*p*-anisylmethylpyrylium derivative, but yields *s*-tri-*p*-anisylbenzene and a red salt containing sulphur which has not been investigated. With suitable modification of the conditions, the new compound can also be obtained from pre-formed *p*-methoxyacetophenone; its preparation is thus analogous to that of mesitylene from acetone.

s-*Tri-*p-*anisylbenzene*, $C_6H_3(C_6H_4\cdot OMe)_3$, crystallises in colourless needles, m. p. 142°. It yields a vivid green, crystalline additive compound with bromine, which, however, is highly unstable at the atmospheric temperature. It is transformed by hydrochloric acid at 160° into s-*tri-*p-*hydroxyphenylbenzene*, m. p. 229°, which yields a *triacetate*, colourless, coarse needles, m. p. 154°. H. W.

A New Phenol in the Essential Oils of the *Leptospermum*. A. R. PENFOLD (*Perf. and Essent. Oil Rec.*, 1921, **12**, 336).—The essential oil obtained from the leaves and terminal branches of *Leptospermum flavescens* contains a phenolic substance varying

in amount from about 1—8%, according to the locality from which the material was collected. The phenol, extracted and purified in the usual way, forms an almost colourless, viscous liquid, possessing a pleasant odour, and giving with ferric chloride in alcoholic solution a brilliant orange-red coloration, and with copper salts an intense blue. It has the following characters: b. p. 145—146°/10 mm., 275—278°/770 mm., $d^{20}=1{\cdot}073$, $\mu_{20}=1{\cdot}5000$, optically inactive. Its composition appears to be represented by the formula $C_{14}H_{20}O_4$, but as no solid crystalline derivatives could be obtained the accuracy of this formula could not be further tested. The phenol, to which the name *leptospermol* is given, strongly resembles tasmanol, a constituent of certain eucalyptus oils, in many of its properties. G. F. M.

The Valency Problem of Sulphur. VI. The Sulphur Analogues of the Aromatic Diazonium Compounds. HANS LECHER and KURT SIMON (*Ber.*, 1921, **54**, [*B*], 2249—2251).—A sulphur analogue, $Ar{\cdot}S_2{\cdot}X$, of the aromatic diazonium compounds is obtained when *o*-nitrothiolbenzene is allowed to react in anhydrous ethereal solution at a low temperature with sulphur dichloride. After removal of a small amount of insoluble by-product, the solution is slowly evaporated under diminished pressure over calcium chloride, and the residue is freed from traces of sulphur chlorides by preservation in a vacuum in the presence of antipyrine. The *compound*, $C_6H_4O_2NS_2Cl$, forms yellow, well-defined crystals, m. p. 62—63° after softening at 55°. It is rapidly decomposed by moist air with the formation of hydrogen chloride. It has a normal molecular weight in freezing benzene. The question of the nomenclature of this and similar compounds is left undecided until the actual analogy of the substances with the diazonium compounds has been examined experimentally. H. W.

The Molecular Transpositions in the Series of Alkylhydrobenzoins and of the Analogous α-Glycols. (MLLE) JEANNE LÉVY (*Bull. Soc. chim.*, 1921, [iv], **29**, 865—878; cf. this vol., i, 233; Tiffeneau and Orékhoff, this vol., i, 243, 565, 566).—In further consideration of the dehydration of aromatic trisubstituted α-glycols, it is suggested that, with dilute sulphuric acid, the reaction is unimolecular, there being no formation of an intermediate product. The dehydration of the same glycols with concentrated sulphuric acid, or in certain cases with phosphoric oxide, will be, at least for the part of the reaction which accompanies the transposition, a bimolecular reaction resulting in the intermediate formation of diethylenic oxides. These oxides, by direct rupture or rupture consecutive to the addition of the reagent, will be transformed into transposed ketones.

These views find support in the behaviour of αβ-diphenylpropan-αβ-diol and of αβ-diphenylbutan-αβ-diol towards sulphuric acid of different strengths, it being possible in each case to isolate the intermediate diethylenic oxide and subsequently to convert it into the ketone. W. G.

Some Retropinacolic Transpositions and the Mechanism of these Transpositions. (MLLE) JEANNE LÉVY (*Bull. Soc. chim.*, 1921, [iv], 29, 878—899).—A more detailed account of work already published (this vol., i, 233). W. G.

Studies of Halogenohydrins and Related Derivatives in the Cinnamic Acid Series. I. JOHN READ and ALBERTA CATHERINE PRITCHARD ANDREWS (T., 1921, **119**, 1774—1786).

The Influence of Boric Acid on the Conductivity of Phenolcarboxylic Acids. J. BÖESEKEN and (MLLE) P. OUWEHAND (*Rec. trav. chim.*, 1921, **40**, 574—577; cf. this vol., i, 843).—The increase in the conductivity of *o*-hydroxy-aromatic acids brought about by adding a solution of boric acid is very great. It may be used to distinguish these acids from their isomerides, whatever the number of hydroxyl groups and their positions with respect to each other. H. J. E.

***m*-Dithiobenzoic Acid.** SAMUEL SMILES and JESSIE STEWART (T., 1921, **119**, 1792—1798).

***o*-Tetrahydro-β-naphthoylbenzoic Acid, its Reduction and Condensation Products.** G. SCHROETER (*Ber.*, 1921, **54**, [*B*], 2242—2248).—The work was undertaken with a view to the discovery of possible substitutes for the fatty acids (cf. Willstätter and Waldschmidt-Leitz, this vol., i, 667).—In consideration of the general instability of tetrahydronaphthalene in the presence of aluminium chloride, it is somewhat surprising to find that it condenses readily with phthalic anhydride in not too dilute benzene solution and in the presence of the catalyst to give a 91% yield of o-*tetrahydro-β-naphthoylbenzoic acid*, colourless needles, m. p. 153—155° (the *ammonium* salt is sparingly soluble in water; the *methyl* ester, m. p. 73—74°, and the *acetyl-lactone*,

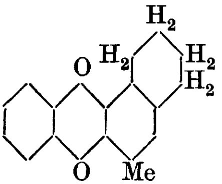
$$\begin{matrix}OAc\\C_{10}H_{11}\end{matrix}\!\!>C<\!\!\begin{matrix}C_6H_4\\O\text{——}\end{matrix}\!\!>CO,$$

colourless needles, m. p. 135°, are described). It is reduced by amalgamated zinc and hydrochloric acid to o-*tetrahydro-β-naphthylmethylbenzoic acid*, colourless crystals, m. p. 126°, the *methyl* ester of which, a colourless liquid, has b. p. 234—235°/15 mm. The latter is converted by hydrogen under pressure at 180—200° in the presence of a nickel catalyst into (?) *methyl ω-decahydro-β-naphthyl*-o-*toluate*, a colourless, viscous liquid, b. p. 222°/15 mm., which is transformed by hydrolysis to a semi-solid *acid* yielding a potassium salt with slight lathering power.

The constitution of *o*-tetrahydro-β-naphthoylbenzoic acid is deduced from the observation that it is converted by fuming sulphuric acid under certain conditions into a mixture of *tetrahydronaphthanthraquinones* (2 : 3-*compound*, yellow needles, m. p. 211°, 1 : 2-*compound*, yellow needles, m. p. 135°) which are oxidised to anthraquinone-2 : 3- and -1 : 2-dicarboxylic acids respectively; the formation of the two anthraquinone compounds is only possible with a β-naphthoyl derivative, but it is remarkable that naphthalene

under similar conditions gives mainly o-α-naphthoylbenzoic acid (cf. Willstätter and Waldschmidt-Leitz, *loc. cit.*).

β-*Methyltetrahydronaphthalene*, a colourless liquid, b. p. 220—222°, prepared by the catalytic hydrogenation of β-methylnaphthalene, is converted by phthalic anhydride and aluminium chloride in the presence of benzene into o-3-*methyl*-5:6:7:8-*tetrahydro*-2-*naphthoylbenzoic acid*, colourless needles, m. p. 160° (the *ammonium* salt is described), which is transformed by fuming sulphuric acid exclusively into the *anthraquinone* derivative (annexed formula), slender, yellow needles, m. p. 119°. From this observation it follows also that β-methylnaphthalene is hydrogenated in the non-methylated nucleus. H. W.



Constituents of the Kawa-root. II. Kawa Resin. W. BORSCHE and A. ROTH (*Ber.*, 1921, **54**, [*B*], 2229—2235).—Previous investigation of the kawa-root (*Piper methysticum*) has shown the presence of methysticin, yangonin, and a viscous, dark brown resin (cf. Borsche and Gerhardt, A., 1915, i, 438). The latter is found to consist for the most part of an ester of kawaic acid; this acid is to be regarded either as α-cinnamylideneacetoacetic acid, $CHPh{:}CH{\cdot}CH{:}CAc{\cdot}CO_2H$, or γ-cinnamylideneacetoacetic acid, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, and, in all probability, as the latter. The nature of the alcoholic component has not been established. Methyl or ethyl alcohol is not, however, present.

Kawa resin is decomposed under all conditions when distilled under diminished pressure, giving a yellow oil, b. p. 150—155°/15 mm., which is catalytically hydrogenated to δ-phenylbutyl methyl ketone. The resin is readily dissolved by hot, aqueous sodium hydroxide solution (10%), and the solution, when cooled, deposits *sodium kawa-ate* in the form of yellow leaflets. The corresponding *acid*, $C_{13}H_{12}O_3$, crystallises in yellow needles, m. p. 164—165°, and is readily decomposed into carbon dioxide and a dark yellow resin which yields considerable amounts of cinnamylideneacetone when distilled. Catalytic hydrogenation of sodium kawa-ate in aqueous solution according to Paal's method leads to the formation of an acid, colourless leaflets, m. p. (indefinite) above 90° (decomp.), which, however, must be almost pure *tetrahydrokawaic acid*, since it passes smoothly when distilled into δ-phenylbutyl methyl ketone (*semicarbazone*, colourless leaflets, m. p. 140—142° when rapidly heated).

Ethyl α-cinnamylideneacetoacetate differs completely from purified kawa-resin in its behaviour under the influence of warm sodium hydroxide (10%). Further, when catalytically hydrogenated and subsequently hydrolysed, it yields immediately carbon dioxide and δ-phenylbutyl methyl ketone instead of tetrahydrokawaic acid. H. W.

Replaceability of the Halogen in Halogen-substituted Phthalic Acids. A. ECKERT and F. SEIDEL (*J. pr. Chem.*, 1921, [ii], **102**, 338—360).—In conjunction with many collaborators,

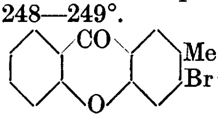
Ullmann (cf., for instance, A., 1907, i, 846) has shown that, in presence of copper, a halogen atom in an organic compound may be readily replaced by various radicles. Thus, condensation of *o*-chlorobenzoic acid with aniline or phenol leads to diphenylamine-*o*-carboxylic acid or *o*-phenoxybenzoic acid, ring closure in these compounds then yielding acridone and xanthone. The authors now find that similar replaceability is exhibited by the halogen atoms in 4 : 6-dibromo*iso*phthalic and 2 : 5-dibromoterephthalic acids, but not by those in 3 : 6-dichloro-*o*-phthalic acid. The chlorine atoms in the last cannot be replaced in this manner by either phenoxyl- or anilino-groups, and if they are forcibly removed by fusion of the compound with potassium hydroxide, a little water and a trace of copper, rearrangement occurs simultaneously, α-resorcylic acid and possibly protocatechuic acid being formed.

4 : 6-*Dibromo*-m-*toluic acid*, $C_8H_6O_2Br_2$, obtained by oxidation of 4 : 6-dibromo-*m*-xylene by means of nitric acid, forms white crystals, m. p. 174°; its *potassium* salt, *methyl* ester, m. p. 43°, b. p. 203—206°/758 mm., and *amide*, $C_8H_7ONBr_2$, white needles, m. p. 188°, were prepared.

4 : 6-*Dibromo*iso*phthalic acid*, prepared by the action of alkaline permanganate on the preceding compound, separates in needles, m. p. 250—254°, and its *methyl* ester in white crystals, m. p. 134°.

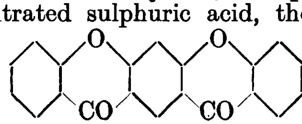
6-*Bromo*-4-*phenoxy*-m-*toluic acid*, prepared by heating 4 : 6-dibromo-*m*-toluic acid with a fused mixture of alkali hydroxide and phenol containing a little copper, forms white crystals, m. p. 137°.

6-*Bromo*-4-*phenoxy*iso*phthalic acid*, obtained when the preceding compound is oxidised by means of alkaline permanganate, crystallises in white needles, m. p. 248—249°.

3-*Bromo*-2-*methylxanthone*, 

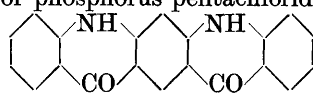
, prepared by heating the preceding acid with concentrated sulphuric acid, crystallises in white needles, m. p. 146°, and dissolves in sulphuric acid to a yellow solution showing a faint green fluorescence.

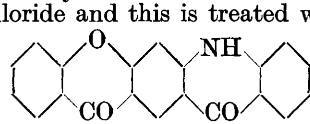
3-*Bromoxanthone*-2-*carboxylic acid*, $C_{14}H_7O_4Br$, obtained by oxidation of the bromomethylxanthone or, in better yield, from 6-bromo-4-phenoxy*iso*phthalic acid, either by treatment with concentrated sulphuric acid or by way of the acid chloride, forms indistinct, white crystals, m. p. 338—344°, and dissolves in concentrated sulphuric acid, giving a yellow solution with faint yellowish-green fluorescence. Its *methyl* ester forms almost white needles, m. p. 154—155°.

4 : 6-*Diphenoxy*iso*phthalic acid*, prepared by heating 4 : 6-dibromo-*iso*phthalic acid with a fused mixture of phenol and potassium hydroxide containing powdered copper, forms crystals, m. p. 256—258°. When heated with concentrated sulphuric acid, the acid is converted into : (1) the *dixanthone*, 

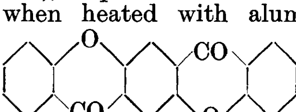
, which crystallises in long, pale yellow needles, m. p. 353°, and

dissolves in concentrated sulphuric acid, giving a yellow solution showing marked yellowish-green fluorescence, but principally (2) a sulphonic acid of the dixanthone, this retaining its sulphonic group with great tenacity. The dixanthone may be more conveniently obtained by heating 4 : 6-diphenoxy*iso*phthalic acid with thionyl chloride; the latter usually yields only acid chlorides and rarely causes such ring-closure. When the diphenoxyphthalic acid is heated slightly above its melting point, it gives the dixanthone and a crystalline compound, m. p. 88—96°, which was not identified. Attempts to reduce the dixanthone resulted in no definite products.

4 : 6-*Dianilinoisophthalic acid*, $C_{20}H_{16}O_4N_2$, prepared by heating 4 : 6-dibromo*iso*phthalic acid with aniline, potassium hydroxide, and copper oxide, crystallises in long, pale red needles, darkening at 265°, m. p. 270—273° (frothing), and dissolves in concentrated sulphuric acid to a colourless solution, which is coloured yellow or yellowish-brown by nitric acid and violet-red by aqueous ferric chloride; it is accompanied by another acid, possibly 6-bromo-4-anilino*iso*phthalic acid, but this was not investigated owing to the difficulty in purifying it. When the dianilino-acid is treated with either thionyl chloride or phosphorus pentachloride, it is converted into the quinacridone, , which crystallises in yellow needles and dissolves in concentrated sulphuric acid to a violet-red solution showing red fluorescence, the colour of this liquid being discharged temporarily by aqueous ferric chloride. When kept fused for some time, the dianilino-acid loses carbon dioxide, yielding *m*-dianilinobenzene.

3-*Anilinoxanthone-2-carboxylic acid*, $C_{20}H_{13}O_4N$, prepared by heating 3-bromoxanthone-2-carboxylic acid with aniline, forms crystals, m. p. 310—313°. When heated above its melting point, this acid loses carbon dioxide and yields 3-*anilinoxanthone*, $C_{19}H_{13}O_2N$, greenish-yellow needles, whilst when it is converted into the acid chloride and this is treated with aluminium chloride, the *compound*, , which forms yellow crystals, is obtained.

2 : 5-*Diphenoxyterephthalic acid*, $C_{20}H_{14}O_6$, prepared from 2 : 5-dibromoterephthalic acid (cf. Claus and Wimmel, A., 1880, 632), separates in white crystals, m. p. 314°. Its chloride, when heated with aluminium chloride, yields the *dixanthone*,

, which forms yellow crystals, and dissolves in concentrated sulphuric acid to a red solution showing a slight blue tinge; this solution exhibits far weaker fluorescence than that of the isomeric dixanthone. T. H. P.

The Application of Hofmann's Reaction to Substituted Phthalimides. TOM SIDNEY MOORE, MURIEL TREGARTHEN MARRACK, and ANNIE KATHLEEN PROUD (T., 1921, **119**, 1786—1791).

Unsaturated Bile Acids. II. An Isomeride of *apo*Cholic Acid. FR. BÖDECKER and H. VOLK (*Ber.*, 1921, **54**, [*B*], 2489—2492; cf. A., 1920, i, 848).—*apo*Cholic acid, obtained by the action of dehydrating agents on cholic acid, is found to be accompanied by an *isomeric acid*, $C_{24}H_{38}O_4$, which crystallises in tasteless, slender, woolly needles, m. p. 259—260° (corr.), $[\alpha]_D^{27}$ +57·3°, decolorises bromine and permanganate, and does not appear to be a secondary product derived from *apo*cholic acid. The *barium* salt ($+6H_2O$) was analysed, and the *methyl* ester, $C_{24}H_{37}O_4Me,MeOH$, forms stout prisms, m. p. 85—90° (frothing), $[\alpha]_D^{25}$ +60·27°, and has the normal molecular weight in boiling methyl alcohol. T. H. P.

***m*-Opianic Acid (4 : 5-Dimethoxy-*o*-aldehydobenzoic Acid).** ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun. (T., 1921, **119**, 1724—1744).

Certain Substances contained in Lichens. G. BARGELLINI and C. MONCADA (*Gazzetta*, 1921, **51**, ii, 173—180).—The following preliminary results have been obtained.

Stictaic acid, extracted from Italian *Sticta pulmonaria* by means of acetone, agrees in properties with the acid obtained by Hesse, from the same lichen grown in Germany (A., 1898, i, 681; 1905, i, 140; 1911, i, 208), its composition being in agreement with the formula $C_{19}H_{14}O_9$. It crystallises in white needles, becomes brown at about 240°, and melts and decomposes at about 260°. In alcoholic solution, it gives a deep violet-red coloration with ferric chloride, but, unlike some other compounds occurring in lichens, it is not decomposed when heated with alcohol in a sealed tube at 150° and its alcoholic solution gives no coloration with calcium hypochlorite. Pyridine dissolves and decomposes the acid, a yellowish-red substance being formed; the action of sulphuric acid yields a red compound, that of nitric acid a yellow compound, and that of alkali carbonates a yellow, crystalline compound, m. p. 215—225° (decomp.). These various compounds are to be investigated. The *acetyl* derivative of stictaic acid crystallises in white needles, m. p. about 230° (decomp.), but the number of acetyl groups in the molecule has not been ascertained.

Stereocaulic acid, obtained from various species of *Stereocaulon*, appears to be identical with stictaic acid. T. H. P.

Citral Series. Optical Determination of the Constitution of Compounds of the Citral Series. E. KNOEVENAGEL and G. OELBERMANN (*J. pr. Chem.*, 1921, [ii], **102**, 305—331; cf. A., 1919, i, 15).—The authors have measured, for a number of citral derivatives, the refractive indices at 20° for the α-, β-, and γ-hydrogen lines and for the yellow D_3-helium line; in consequence of the tendency to undergo polymerisation and oxidation exhibited by compounds of this series, the measurements were made on liquids

freshly distilled in a vacuum. From the values obtained for the molecular refractions conclusions are drawn as to the constitutions of certain of the compounds. The effects produced on the refractive indices by storage of the compounds at $-190°$, $-80°$, or the ordinary temperature were examined.

Citral, consisting of two isomerides, which are probably stereoisomerides, contains the conjugated system $\cdot CR\!:\!CH\cdot CH\!:\!O$; according to Eisenlohr (*Spektrochemie organischer Verbindungen*, 1912, 126), the latter gives the specific normal exaltation $E\Sigma_{refr.} = 1{\cdot}25$ and $E\Sigma_{disp.} = 45\%$, which are in good agreement with the authors' results.

ψ-Ionone, according to Tiemann's formula for citral, contains the grouping $\cdot CR\!:\!CH\cdot CH\!:\!CH\cdot CR\!:\!O$, for which Eisenlohr (*op. cit.*, 134) gives $E\Sigma_{refr.}$ somewhat above $2{\cdot}7$ and $E\Sigma_{disp.}$ above 100%; these values agree well with those now obtained. The refraction of α- and β-ionones has been investigated by Auwers and Eisenlohr (A., 1911, ii, 781, 782; cf. Eisenlohr, *op. cit.*, 127, 134).

For ψ-ionone acetate only a cyclic constitution appears possible. Taking the formula $CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe\!:\!CH\cdot CH\!:\!CH\cdot CO\cdot CH_3$ for ψ-ionone, it may be assumed that the acetyl group of the acetic anhydride becomes attached to the carbonylic oxygen and the acetoxy-group to the carbon atom in the θ-position, simultaneous displacement of one double linking occurring with formation of an intermediate compound of the formula

$$CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe\!:\!CH\cdot CH(OAc)\cdot CH\!:\!CMe\cdot OAc.$$

In this, the catalytic action of the ferric chloride used in preparing the compound might result in ring closure between either the γ- and θ- or the ϵ- and κ-carbon atoms. In the former case, the compound having the structure $CH_2{<}{\begin{smallmatrix}CH_2\cdot C(:CMe_2)\\ CMe\!=\!=\!=\!CH\end{smallmatrix}}{>}CH\cdot CH\!:\!CMe\cdot OAc$, would arise, and the theoretical exaltation for such a compound agrees best with the actual value. It is possible that isomeric ψ-ionone acetates exist, as the freshly-prepared compound boils within wide limits.

The values found for the molecular refraction of *iso*-ψ-ionone indicate the formula to be probably $CH_2{<}{\begin{smallmatrix}CH_2\cdot C(:CMe_2)\\ CMe\!=\!=\!=\!CH\end{smallmatrix}}{>}CH\cdot CH_2Ac$, but possibly $CH_2{<}{\begin{smallmatrix}CH_2\cdot C(CHMe_2)\\ CMe\!=\!=\!=\!CH\end{smallmatrix}}{>}C\cdot CH_2Ac$. The former of these two structures was attributed by Knoevenagel to α-*iso*ionone, which, however, exhibits normal optical values.

iso-ψ-Ionone yields the same semicarbazone, $C_{14}H_{23}ON_3$, m. p. 169°, as ψ-ionone acetate.

When heated with zinc chloride at 200°, *iso*-ψ-ionone yields a hydrocarbon, $C_{13}H_{18}$, b. p. 135—145°/21 mm., d_4^{20} 0·9373, which may have one of various structures, between which the available optical and chemical data are insufficient to decide.

Ethyl citrylideneacetoacetate (α-ester) is difficult to obtain pure, as it readily undergoes transformation into the β-ester, but the optical constants obtained indicate the probable accuracy of the structural formula already given (A., 1919, i, 15).

In the case of *α-iso*ionone, the method of preparation and the normal optical data are in agreement with the view that the semicyclic double linking has somehow wandered into the nucleus, giving a compound of the constitution $CH_2{<}{\substack{CH{:}CPr^{\beta}\\ CMe{:}CH}}{>}CH{\cdot}CH_2Ac$.

For ethyl β-citrylideneacetoacetate the normal optical data and the transformations into the β-*iso*- and the β-*pseudo*-esters agree best with the structure $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}C{:}CH{\cdot}CHAc{\cdot}CO_2Et$.

For the hydrocarbon, $C_{13}H_{18}$, obtained by the action of zinc chloride, the constitution $\begin{matrix} CMe{\cdot}CH_2{\cdot}CH{-}{-}CH{:}CMe \\ \| \qquad\qquad | \qquad\quad | \\ CH{-}{-}CH_2{\cdot}CH{\cdot}CMe{:}CH \end{matrix}$ was proposed (*loc. cit.*), but this is not in accord with the refractive data and the boiling point. Better agreement is shown by the structure $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}C{\lessdot}{\substack{CH{:}CMe\\ CH{-}CH}}{\gtrdot}CH$.

The formula previously given (*loc. cit.*) for β-ψ-ionone, which exhibits normal refractive constants, is probably accurate. The same is the case with ethyl β-*iso*citrylideneacetoacetate, the expected absence of exaltation being virtually confirmed experimentally. Moreover, for β-*iso*ionone, normal optical data are obtained, these being in agreement with the structure previously suggested (*loc. cit.*). T. H. P.

The Crystalline-liquid Properties of α-Unsaturated Ketones. D. VORLÄNDER (*Ber.*, 1921, **54**, [*B*], 2261—2264).—The crystalline-liquid properties of dianisylidene*cyclo*hexanone recorded by Müller (this vol., i, 674) have been described previously by the author (A., 1907, ii, 337; 1908, ii, 22). In the case of *pp'*-diethoxybenzylidene*cyclo*hexanone (Huth, *Diss.*, Halle, 1909), the region of existence of the crystalline-liquid is somewhat greater, the transition points lying at 145° and 176°. In the case of derivatives of *cyclo*hexanone, the side chain is of considerable influence, the presence of the methyl radicle having a decided hindering effect. From a considerable number of examples it is shown that the presence of the group in the para- or meta-position renders the corresponding enantiotropic forms monotropic crystalline-liquid whilst 2-methyl*cyclo*hexanone does not yield crystalline-liquid arylidene compounds. Contrary to Müller's statement (*loc. cit.*), dianisylidene*cyclo*pentanone gives an anisotropic melt.

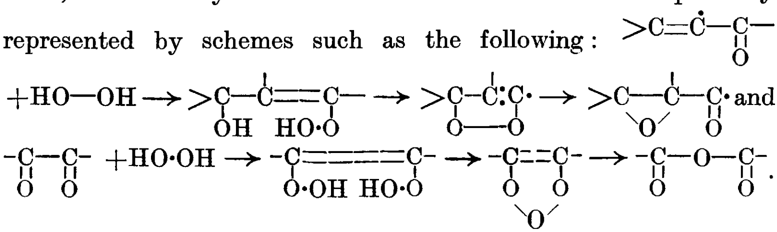
In general, the crystalline-liquid properties of α-unsaturated ketones are not very marked, as is shown by the relatively small regions of existence of the enantiotropic forms and the absence of the phenomenon in the benzylidene and cinnamylidene derivatives. Comparison of arylidene cyclic ketones with non-cyclic α-unsaturated ketones (which are never or but very seldom crystalline-liquid) shows that the presence of the ring enhances the crystalline-liquid properties and that the six-membered ring has a greater influence than that composed of five atoms. It is remarkable that meta-compounds are found among the cyclic derivatives, whereas crystalline-liquid derivatives of aromatic meta-substitution products in the middle of an extended molecule have not yet been observed.

Only when the central portion of the molecule is very strongly developed linearly, for example, in *pp′*-derivatives of diphenyl and in *pp′*-diaminoazo-compounds, can almost any meta- or ortho-substituent be introduced into the molecule without completely destroying the crystalline-liquid condition. H. W.

Studies in the *n*-Butyl Series. I. Aryl *n*-Propyl Ketones. GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM (T., 1921, **119**, 1879—1893).

Action of Alkaline Hydrogen Peroxide on Unsaturated Compounds. ERNST WEITZ and ALFRED SCHEFFER (*Ber.*, 1921, **54**, [*B*], 2327—2344).—It has been shown previously (Weitz, A., 1919, i, 290—291) that 9-benzylideneanthrone and 1 : 2-diphenyl-indene-3-one are converted by hydrogen peroxide in the presence of sodium hydroxide solution into colourless oxides. A similar, extremely ready reaction occurs with αβ-unsaturated ketones; the initial product, if isolable, has the composition ketone + 1 atom of oxygen, and the identity of the substances obtained from benzylideneacetophenone, *p*-chlorobenzylideneacetophenone, and *p*-nitrobenzylideneacetophenone with the products obtained by Widman (A., 1913, i, 1220; 1916, i, 406), Bodforss (A., 1917, i, 223), and Jörländer (A., 1917, i, 222) by the action of the substituted benzaldehydes on ω-bromoacetophenone leaves no doubt that they are substituted ethylene oxides. Alkaline hydrogen peroxide solution does not appear to react with the carbonyl or ethylene group alone, but with the combination of the two in the conjugated system, :C:Ċ·C:O, as it occurs in unsaturated ketones or aldehydes. αβ-Unsaturated acids are relatively stable towards the reagent.

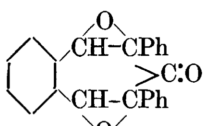
The observations have been extended to other substances containing conjugated bonds. Diolefines and substances such as sorbic acid do not exhibit any striking reactivity. 1 : 2-Diketones, on the other hand, react very readily, passing directly into the corresponding acids without permitting isolation of the oxide formed intermediately. α-Keto-carboxylic acids, on the other hand, are relatively stable. The course of the reactions is probably represented by schemes such as the following:



All the ketoxido-compounds have the property of liberating iodine from potassium iodide and acetic acid with re-formation of the unsaturated ketone. In general, also, they give intensely brownish-yellow solutions when heated to boiling with aqueous alkalis which yield almost colourless precipitates when acidified; the

latter re-dissolve in alkali hydroxide solutions, yielding the original colorations.

The following individual substances are described: β-*acetyl-α-phenylethylene oxide*, $\underset{\diagdown O \diagup}{PhCH{\cdot}CHAc}$, colourless leaflets, m. p. 52—53°, obtained together with a liquid *isomeride* from benzylideneacetone in aqueous methyl-alcoholic solution; β-benzoyl-α-phenylethylene oxide (cf. Widman, *loc. cit.*), colourless leaflets, m. p. 90°; β-benzoyl-α-*p*-nitrophenylethylene oxide, colourless leaflets, m. p. 150° (Bodforss, *loc. cit.*, gives 148°); β-benzoyl-α-*p*-chlorophenylethylene oxide, colourless needles, m. p. 80—81° (Bodforss, m. p. 79—80°); β-*benzoyl*-α-o-*chlorophenylethylene oxide*, crystalline aggregates, m. p. 77° (from o-*chlorostyryl methyl ketone*, pale yellow crystals, m. p. 52—53°); β-*benzoyl*-α-p-*methoxyphenylethylene oxide*, colourless leaflets, m. p. 87°; α-*acetyl*-β-*methylpropylene oxide*, b. p. 44—48°/15 mm.; β-*benzoyl*-α-*styrylethylene oxide*, $\underset{\diagdown O \diagup}{CHPh{:}CH{\cdot}CH{\cdot}CH{\cdot}Bz}$, colourless needles, m. p. 89°; 1 : 2-*diphenylindene*-3-*one oxide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CPh}{CO-}{>}CPh$ (with O bridging CPh and CPh), short needles, m. p. 141° after becoming red at 130°; terephthalylideneacetophenone dioxide, $C_6H_4(\underset{\diagdown O \diagup}{CH{\cdot}CHBz})_2$, leaflets, m. p. 195° after softening at 175° [Bodforss (A., 1918, i, 229) gives m. p. 220—222°, the difference being probably due to the existence of *cis-trans*-isomerism]; *diphenylbenzo*cyclo*heptadianone dioxide* (annexed formula), prisms, m. p. 167—168°. H. W.



Transformations of Ketoxido-compounds. Formation of β-Ketonic Aldehydes from αβ-Unsaturated Ketones. Ernst Weitz and Alfred Scheffer (*Ber.*, 1921, **54**, [*B*], 2344—2353; cf. preceding abstract).—The action of acetic acid and mineral acid on ketoxide compounds leads in certain cases to the production of β-ketoaldehydes, but in more complex instances its exact course has not been fully elucidated. It is shown, however, to depend to some extent on the nature of the mineral acid used.

β-Acetyl-α-phenylethylene oxide, $O{<}\genfrac{}{}{0pt}{}{CHPh}{CHAc}$, is converted by a solution of hydrogen chloride in glacial acetic acid into an oily *chlorohydrin* which slowly evolves hydrogen chloride spontaneously at the atmospheric temperature and passes into α-*phenylacetoacetaldehyde*, CHPhAc·CHO, or, more probably, *hydroxymethylenebenzyl methyl ketone*, OH·CH:CPh·COMe, m. p. 67—68°. The substance is somewhat unstable at the atmospheric temperature, gives an intense, reddish-violet coloration with ferric chloride, a greenish-yellow, crystalline *copper* salt, and a (?) *phenylhydrazone*, $C_{16}H_{16}ON_2$, almost colourless, ill-defined leaflets, m. p. 171°. β-Benzoyl-α-phenylethylene oxide gives only ill-defined products with acetic acid and hydrogen chloride, but is transformed by acetic and concentrated sulphuric acids into formyldeoxybenzoin

(Wislicenus and Ruthing, A., 1911, i, 303). The transformation $O<\begin{matrix}CHPh\\ | \\ CHBz\end{matrix} \longrightarrow CHPh\cdot Bz\cdot CHO$, is thus analogous to the pinacolin transformation or, more precisely, to the conversion of hydrobenzoin into diphenylacetaldehyde. If the terminal carbon atom of the oxide group is not attached to a hydrogen atom, as in αα-dimethyl-β-acetylethylene oxide, a 1 : 2-diketone appears to be formed.

1 : 2-Diphenylindene-3-one oxide, $\begin{matrix}C_6H_4\cdot CPh\\ | \quad\quad | \\ CO\text{---}CPh\end{matrix}>O$, is converted by hydrogen chloride or hydrogen bromide and glacial acetic acid into a "*hydrate*," $C_{21}H_{16}O_3$, m. p. 160—168° after darkening at about 155°, or a mixture of this substance and the corresponding *lactone*, straw-yellow prisms, m. p. 168—169°; the latter substance, $C_{21}H_{14}O_2$, is also prepared from the oxide and sulphuric and acetic acids. It is converted by aqueous alcoholic alkali hydroxide solution into the *acid*, $C_{21}H_{16}O_3$, leaflets, m. p. 142° (decomp.) after softening at 139°. The constitution of the hydrate (i), lactone (ii), and acid (iii) have not been placed beyond doubt, but the following formulæ are highly probable. The

$$C_6H_4<\begin{matrix}CHPh\cdot CPh\cdot OH\\ \quad\quad\quad | \\ CO\text{----}O\end{matrix} \qquad C_6H_4<\begin{matrix}CPh\colon CPh\\ \quad\quad | \\ CO\text{--}O\end{matrix} \qquad C_6H_4<\begin{matrix}CHPh\cdot COPh\\ CO_2H\end{matrix}$$

(I.) (II.) (III.)

"hydrate" is transformed by sodium hydroxide into a neutral yellow *product*, $C_{21}H_{14}O_2$ or $(C_{21}H_{14}O_2)_2$, m. p. 129°, which is possibly 3 : 3-diphenylindan-1 : 2-dione. H. W.

Dinaphtha-1 : 7 : 1′ : 7′-diquinone. GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1921, **119**, 1707—1714).

Preparation of Compounds of the Anthraquinone Series. FREDERICK WILLIAM ATACK and GEORGE WILLIAM CLOUGH (Brit. Pat. 169732).—α-Chloro- or α-bromo-anthraquinones are converted into β-halogen derivatives by heating with concentrated sulphuric acid for some hours at about 200°. As the halogen atom always takes up the meta-position with respect to its original position, the reaction is, of course, limited to those anthraquinone derivatives in which this particular β-position is unoccupied. Further, those derivatives are excluded which are decomposed by hot sulphuric acid such as 4-chloro-1-hydroxyanthraquinone, in which case the dihydroxy-compound is produced, or 4-chloro-1-amino-anthraquinonesulphonates, in which the chlorine atom is expelled. With these exceptions, the orientating action of sulphuric acid appears to be specific and the reaction with α-halogen-anthraquinones a general one. For example: 50 parts of 1-chloroanthraquinone are heated with 920 parts of sulphuric acid (*d* 1·84) at 200—205° for nine hours. The reaction mixture is poured into water and the precipitated 2-chloroanthraquinone recrystallised from acetic acid. G. F. M.

Octachloroanthraquinone. ALFRED ECKERT (*J. pr. Chem.*, 1921, [ii], **102**, 361).—The action of antimony pentachloride on

anthraquinone in presence of iodine yields, in addition to the compounds already described (A., 1915, i, 565), also *octachloroanthraquinone*, $C_{14}O_2Cl_8$, which crystallises in yellow needles, m. p. above 360°. T. H. P.

The Dibromoanthraquinone Used in the Synthesis of Alizarin. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 717—718).—It is shown that the dibromoanthraquinone used by Graebe and Liebermann in their synthesis of alizarin was 2 : 3-dibromoanthraquinone. W. G.

Preparation of α-Aminoanthraquinone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 169667).—α-Aminoanthraquinone may be obtained by heating α-anthraquinonesulphonic acid with ammonia under pressure in presence of the sulphonic acid of an aromatic nitro-compound. For example, if 165 parts of potassium α-anthraquinonesulphonate, 500 parts of 24% aqueous ammonia, and 60 parts of sodium nitrobenzenesulphonate are heated for twelve hours at 160—165°, and the contents of the autoclave are then allowed to cool, a yield of 80% of the theoretical of pure crystalline α-aminoanthraquinone is directly obtained, and a quantity of anilinesulphonic acid may be recovered from the filtrate. G. F. M.

Derivatives of 2-Methylanthraquinone. ALFRED ECKERT and GERTRUD ENDLER (*J. pr. Chem.*, 1921, [ii], **102**, 332—337).—The preparation of 1-methoxy-2-methylanthraquinone from 1-nitro-2-methylanthraquinone according to D.R.-P. 75054 is difficult, and this compound is obtainable more readily by heating 1-chloro-2-methylanthraquinone with methyl alcoholic potassium hydroxide in a sealed tube at 80°. It crystallises in pale yellow needles, m. p. 152—153°.

1-*Methoxyanthraquinone-2-carboxylic acid*, $C_{16}H_{10}O_5$, prepared either by oxidising the preceding compound in acetone solution by means of permanganate or, better, by boiling 1-nitroanthraquinone-2-carboxylic acid with methyl alcoholic potassium hydroxide, forms yellow needles, m. p. 250—253°.

5 : 8-*Dichloro-2-methylanthraquinone*, $C_{15}H_8O_2Cl_2$, prepared by treating 3 : 6-dichlorophthalic anhydride in toluene with aluminium chloride and heating the resulting dichlorotoluoylbenzoic acid, m. p. 160—161°, with sulphuric acid, crystallises in yellow needles, m. p. 242—244°. When oxidised with chromium trioxide and sulphuric acid, it yields

5 : 8-*Dichloroanthraquinone-2-carboxylic acid*, $C_{15}H_6O_4Cl_2$, which forms yellow needles, m. p. above 390°.

Tetrachlorotoluoylbenzoic acid, $C_{15}H_8O_3Cl_4$, prepared from tetrachlorophthalic anhydride, forms crystals, m. p. 142°, and when heated with fuming sulphuric acid yields an acid *compound* which crystallises in almost colourless needles, m. p. 281° (slight browning), has the molecular weight 403, and contains 7·6% of sulphur and 33·5% of chlorine.

5 : 6 : 7 : 8-*Tetrachloro-2-methylanthraquinone*, $C_{15}H_6O_2Cl_4$, ob-

tained like the dichloro-compound, crystallises in yellow needles, m. p. 195—196°.

Tetrachlorobenzophenonedicarboxylic acid, $C_{15}H_6O_5Cl_4$, prepared by the action of permanganate on tetrachlorotoluoylbenzoic acid in presence of sodium carbonate, forms white crystals, m. p. 280°, and when treated with sulphuric acid undergoes condensation to

5 : 6 : 7 : 8-*Tetrachloroanthraquinone-2-carboxylic acid*, $C_{15}H_4O_4Cl_4$, which crystallises in pale yellow needles, m. p. 295—296°.

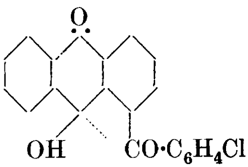
T. H. P.

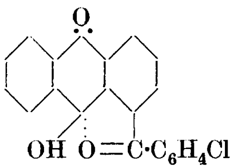
New Class of Compounds with Tervalent Carbon. I. ROLAND SCHOLL (*Ber.*, 1921, **54**, [*B*], 2376—2388).—By the action of aluminium or copper on concentrated sulphuric acid, or of zinc dust and ammonia on 1-benzoylated anthraquinones, Schaarschmidt (A., 1915, i, 566, 696; 1916, i, 408) obtained deep violet-blue compounds exhibiting pronounced fluorescence in various solvents. The author has now investigated these compounds and finds that they are not pinacones, as Schaarschmidt supposed, but representatives of a new class of compounds containing tervalent carbon.

[With HERBERT HÄHLE.]—The reduction product of 1-*p*-chlorobenzoylanthraquinone, for which Schaarschmidt gave m. p. 220—222°, may be obtained crystalline in stable, curved, violet-blue needles, m. p. 253°. In solution in organic solvents it undergoes oxidation in the air and free chromic acid converts it into 1-*p*-chlorobenzoylanthraquinone. Measurements of the molecular weight in boiling nitrobenzene solution demonstrate the inaccuracy of Schaarschmidt's doubled formula. In nitrobenzene, the compound unites with bromine, the proportion of the latter combined indicating for the compound the formula $C_{21}H_{12}O_3Cl$, which is that of a compound containing tervalent carbon.

As regards the position assumed by the atom of reducing hydrogen, Schaarschmidt assumed that the addition occurred at the carbonyl of the chlorobenzoyl residue. That this is not the case and that the double ketonic group of the anthraquinone is more readily attacked by the reducing agents employed than is the carbonyl group of simple aromatic ketones is shown by the following observations. (1) Anthraquinone and many of its derivatives are easily reduced by concentrated sulphuric acid and powdered metal in the cold or at a gentle heat; thus, 1 : 1′-dianthraquinonyl yields *meso*benzdianthrone (Scholl, Mansfeld, and Potschiwauscheg, A., 1910, i, 494). (2) When reduced by means of aluminium bronze and concentrated sulphuric acid, 2-*p*-toluoylanthraquinone yields 2-*p*-toluoyl-9-oxanthrone and 2-*p*-toluoylanthranol (Schaarschmidt and Irineu, A., 1916, i, 408). (3) 1-Benzoyl*allo*chrysoketone, which is free from the reactive quinone carbonyls, appears to yield no reduction product with concentrated sulphuric acid and powdered aluminium or copper (Schaarschmidt, A., 1916, i, 47). It is hence considered justifiable to conclude that, in the formation of the violet reduction product, $C_{21}H_{12}O_3Cl$, from 1-*p*-chlorobenzoylanthraquinone, the hydrogen atom passes to one of the quinone carbonyl groups.

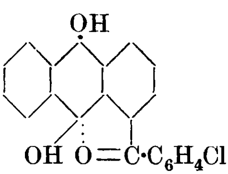
In anthraquinone derivatives with negative substituents in position 1, the carbonyl in the 9-position adjacent to the substituents appears to be more highly reactive than that in the 10-position. Thus, in the reduction of 1 : 1′-dianthraquinonyl to *meso*benzdianthrone, the latter is obtained in almost quantitative yield. From these considerations the violet reduction product is regarded as a 1-*p*-chlorobenzoyl-9-oxanthronyl with a tervalent carbon atom, as shown in the annexed formula. That the reduction comes to a halt at this stage instead of proceeding to the formation of oxanthrone probably finds its cause in the relationship existing between the carbon atom in the 9-position and the 1-benzoyl group. The remaining affinity of the 9-carbon atom may be largely satisfied by the residual affinity of the oxygen of the benzoyl group, with formation of the intramolecular ketone additive product shown annexed (I).



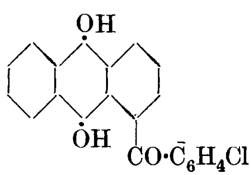


(I.)

Characteristic of compounds of this class is the possession of a conjugated, tervalent carbon atom co-ordinatively united in an inner complex ring. Such compounds are comparable with the additive products formed by hydrocarbons, and especially by hydroxylated aromatic hydrocarbons with ketones according to the structure given by Pfeiffer, or with the quinhydrones. As regards the behaviour of the chlorobenzoyloxanthronyl towards alkaline hyposulphite (Schaarschmidt, *loc. cit.*), it may be assumed that one hydrogen atom is taken up without rupture of the co-ordinative linking or opening of the complex ring. The resulting inner-complex chlorobenzoylanthraquinol (II) reverts to the blue compound (I) in the air but in the alkaline solution undergoes dissociation, completely but less slowly than it is formed, into the stable "open" chlorobenzoylanthraquinol (III), which is oxidised in the air to 1-*p*-chlorobenzoylanthraquinone.



(II.)



(III.)

The reaction of the compound with three atoms of bromine is readily explained by the co-ordination formula. The co-ordinative linking is broken down by addition of 2 bromine atoms, the liberated principal valency of the carbon of the original chlorobenzoyl carbonyl being then saturated by the third bromine atom, with formation of a bromocarbinol hypobromite,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}C_6H_3{\cdot}CBr(OBr){\cdot}C_6H_4Cl,$$

comparable with the alkyl hypochlorites.

The benzoyloxanthronyls are oxymethyls and, as they correspond

with Schlenk's metal ketyls (A., 1913, i, 1205), may be designated hydroketyls. Their discovery and stability dispose finally of Schmidlin's conception of the metal ketyls as loose additive compounds of the metals with ketones analogous to the coloured molecular compounds of ketones with metallic chlorides (" *Das Triphenylmethyl*," 1914, 186).

With *p*-benzoquinone the bluish-violet chlorobenzoyloxanthronyl forms an additive compound which crystallises in faintly yellow, rhombohedral plates, is comparable with the quinol *bis*-triphenylmethyl ether obtained by Schmidlin, Wohl, and Thommen (A., 1910, i, 377) from triphenylmethyl and *p*-benzoquinone, and in solution dissociates into its constituents below 100°, giving the characteristic colour of the chlorobenzoyloxanthronyl.

1 *p-Chlorobenzoyl-9 : 10-di-*p*-bromobenzoylanthraquinol*,

$$C_6H_4{<}{\substack{C(O\cdot CO\cdot C_6H_4Br)\\ C(O\cdot CO\cdot C_6H_4Br)}}{>}C_6H_3\cdot CO\cdot C_6H_4Cl,$$

prepared by treating either 1-*p*-chlorobenzoyl-9-oxanthronyl or 1-*p*-chlorobenzoylanthraquinone in alkaline sodium hyposulphite solution under hydrogen with ethereal *p*-bromobenzoyl chloride (cf. Scholl, Mansfeld, and Potschiwauscheg, *loc. cit.*), forms a pale brown powder. T. H. P.

The Products of Reduction of Dimethylcampholamide. A. Haller and (Mme) P. Ramart (*Compt. rend.*, 1921, **173**, 682—685).—When reduced by sodium in absolute alcohol, dimethylcampholamide gives a small amount of dimethylcampholylamine together with an indefinite compound, which, during purification, undergoes dehydration, giving *dimethylcampholonitrile*,

$$CHMe_2\cdot C_8H_{14}\cdot CN,$$

b. p. 245—247° or 131—133°/14 mm.; $[\alpha]_D^{25}$ +3·2°. On hydrolysis with sulphuric acid, the nitrile gives the original amide, and on reduction with sodium and absolute alcohol readily gives *dimethylcampholylamine*, $CHMe_2\cdot C_8H_{14}\cdot CH_2\cdot NH_2$, b. p. 123—124°/20 mm.; $[\alpha]_D^{25}$ +30·1°, which is very basic and gives a *sulphate*, a *hydrochloride*, and a *platinichloride*.

Dimethylcampholyl chloride reacts with absolute alcohol, giving *ethyl dimethylcampholate*, b. p. 138°/24 mm.; $[\alpha]_D^{25}$ +37·2°; and with sodium phenoxide, giving *phenyl dimethylcampholate*, b. p. 190—195°/30 mm., and the latter ester on reduction with sodium and absolute alcohol yields *dimethylcampholyl alcohol*,

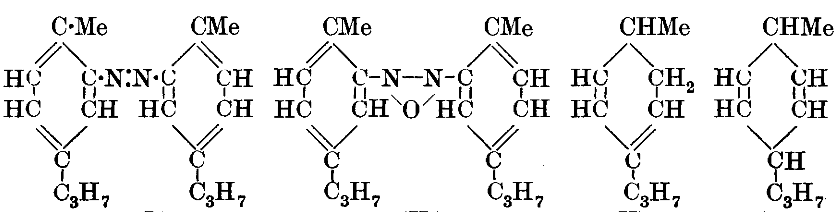
$$CHMe_2\cdot C_8H_{14}\cdot CH_2\cdot OH,$$

b. p. 139—140°/20 mm.; $[\alpha]_D^{24}$ +32°. W. G.

A New Method for the Resolution of Asymmetric Compounds. Akira Shimomura and Julius Berend Cohen (T., 1921, **119**, 1816—1825).

Chenopodium Oil. Thomas Anderson Henry and Humphrey Paget (T., 1921, **119**, 1714—1724).

The Essential Oil of *Mosla japonica*, Maxim. YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, 769—786; cf. Haneda, *ibid.*, 1889, No. 92; Shimoyama, A., 1893, ii, 181; Hoshino, *J. Chem. Ind., Japan*, 1919, **22**, 557).—The essential oil of *Mosla japonica*, Maxim, freed from *p*-cymene, was separated by repeated fractional distillation into a terpene fraction, b. p. 173—175°, or 59—60°/10 mm., and a sesquiterpene fraction, b. p. 125—128°/10 mm. From the former, a new terpene, $C_{10}H_{16}$, *moslene*, was isolated, which resembles, but is not identical with, the crithmene of Francesconi and Sernagiotto (A., 1913, i, 636). By passing hydrogen chloride into a cooled ethereal solution of the terpene, it yields a *hydrochloride*, $C_{10}H_{16},2HCl$, m. p. 51°; this suggests the presence of α-terpinene and the formation of $C_{10}H_{16}(OH)_4$, m. p. 235—238°, by oxidation with potassium permanganate, indicates the presence of γ-terpinene. The terpene yields a *nitrosochloride*, $C_{10}H_{16}ONCl$, white crystals, m. p. 111°, which by treatment with piperidine in alcoholic solution is converted into the *nitrolpiperidide*, lustrous, small plates, m. p. 142—143°, and by heating with aniline, into the *nitrolanilide*, small prisms, m. p. 126—128°. *Moslene nitrosate*, forming needles, m. p. 114°, is obtained by adding a mixture of glacial acetic acid and nitric acid (*d* 1·4) to a cooled mixture of the terpene, amyl nitrite, and glacial acetic acid. By warming the nitrosochloride with sodium ethoxide, an *azoxy*-compound, m. p. 52—53°, and an *azo*-compound, orange-yellow crystals, m. p. 85—87°, are formed. On reduction with zinc dust and glacial acetic acid, the azo- or azoxy-compound gave white crystals, of the composition $C_{20}H_{24}(NH_2)_2,2HCl$, which changes its colour at about 262° and decomposes at 280—292°; this gives, with chloroauric acid, a blood-red coloration and then a greyish precipitate. The platinichloride forms yellow grains, and does not melt below 300°. By warming 2-nitro-*p*-cymene (*Shimmels Bericht*, 1919, 130) with zinc dust in sodium ethoxide solution on a water-bath, an azo-compound is produced which is identical with that obtained from moslene nitrosochloride. The constitution of the azo-compound therefore corresponds with (I) and that of the azoxy-compound with (II); it follows that the new terpene, moslene, is a dihydro-*p*-cymene. There are theoretically five isomeric dihydro-*p*-cymenes, three of which are known. Moslene must therefore have the constitution (III) or (IV).



(I.) (II.) (III.) (IV.)

From the sesquiterpene fraction, caryophyllene was obtained and identified by the formation of its nitrosochloride, m. p. 161° (the

thoroughly purified nitrosochloride melts at 177°), nitrosate, m. p. 147—148°, and alcohol, m. p. 82—84°. K. K.

Occurrence of Moslene in Essential Oils containing *p*-Cymene. YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, No. **475**, 786—790).—As the author has isolated a new terpene, moslene, from the essential oil of *Mosla japonica*, Maxim (cf. preceding abstract), its presence was sought for in other essential oils containing *p*-cymene, and was proved in the terpene fractions of ajowan oil (from the fruits of *Ptychotis Ajowan*) and the oil of *Mosla grosseserrata*, Maxim (cf. Murayama, A., 1920, i, 624) by the formation of the nitrosochloride, nitrosopiperidide, and nitrosate respectively. K. K.

The Solubility of some New Resins. P. NICOLARDOT and CH. COFFIGNIER (*Bull. Soc. chim.*, 1921, [iv], **29**, 917—921).—The solubilities of the resins from *Hopea ricopei*, and *Aucoumea Klaïneana*, and of Dammar Cambodge, and light red Dammar (*Thorea vulgaris*) resins in ethyl, methyl, and amyl alcohols, ether, chloroform, benzene, acetone, turpentine, carbon tetrachloride, benzaldehyde, aniline, and amyl acetate are given. W. G.

The Solubility of some Resins from Cochin-China. P. NICOLARDOT and CH. COFFIGNIER (*Bull. Soc. chim.*, 1921, [iv], **29**, 921—932).—Using the same solvents (cf. preceding abstract), the authors have determined the solubilities of the resins of *Hopea odorata*, *Hopea dealbata*, *Shorea vulgaris*, *Shorea hypochra*, *Thorea thorelli*, *Hopea pierrei*, *Anisoptera*, *Natica astrotica*, and the resin from the Chinese pine. W. G.

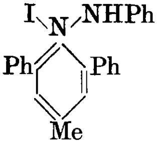
The Relative Activity of Various Allotropic Forms of Sulphur towards Caoutchouc. D. F. TWISS and F. THOMAS (*J. Soc. Chem. Ind.*, 1921, **40**, 48—50T).—Mixtures of plantation rubber with ordinary powdered sulphur and with insoluble sulphur respectively, with the additional presence of 1% of aldehyde-ammonia as catalyst, were vulcanised at 98°, 108°, and 118°. A mixture of synthetic rubber with sulphur was vulcanised at 168°, 178°, and 188°. From the relative rate of vulcanisation in the first set of experiments and the temperature coefficient of the chemical reaction in the second set, the conclusion is drawn that although $S\mu$, as a vulcanising agent, is a little less active than $S\lambda$ or $S\pi$, the difference is surprisingly small. D. F. T.

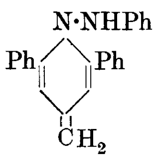
The Discontinuity of Vulcanisation in the Presence of Organic Accelerators. D. F. TWISS (*J. Soc. Chem. Ind.*, 1921, **40**, 242—248T).—When a mixture of natural caoutchouc (90) and sulphur (10) is heated with the additional presence of zinc oxide (1) and hexamethylenetetramine (0·5—2·5), the course of the vulcanisation process, as indicated by the gradual physical alteration in the caoutchouc, is not continuous (see Twiss and Howson, A., 1920,

i, 751). The temporary softening effect which succeeds the initial period of normal alteration is probably due to a "depolymerising" effect by the hexamethylenetetramine. By reducing the proportion of sulphur in the mixture, it is possible to accentuate this effect and render it more persistent. This effect of hexamethylenetetramine is also observable in the absence of zinc oxide, a higher proportion of combined sulphur than the normal being necessary to produce a condition of over-vulcanisation. Indications of a similar phenomenon are given in a milder degree by many other vulcanisation catalysts. In the presence of more zinc oxide the positive effect of such catalysts is increased and the inverse effect is less evident. On the other hand, the activity of other catalysts is but little influenced by zinc oxide; a glycerol solution of potassium hydroxide, for instance, is scarcely affected by the presence of zinc oxide or by previous saturation with hydrogen sulphide. D. F. T.

Saponins. IV. The Saponins of the Nuts of *Pseudophœnix Vinifera*, Beccari, and their Magnesium and Calcium Salts. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1921, **40**, 542—552; cf. A., 1917, i, 41, 70).—These saponins belong to the group which is precipitated neither by normal nor by basic lead acetate, but by the basic acetate in presence of ammonia. They exist partly free and partly as compounds of calcium and magnesium. Their complete hydrolysis is a matter of some difficulty; the resulting saccharides are rhamnose, lævulose, and *d*-galactose. Pentoses, fucose, dextrose, *d*-mannose, and acids of the glycuronic group are absent. Sapogenins produced by hydrolysis constitute about 40% of the saponin and consist of a mixture of crystalline and amorphous substances. Two have been isolated in crystalline form, m. p. 328° and 215—216° respectively. The formula of the latter is $C_{20}H_{32}O$, and the substance is of the nature of phytosterol. The author considers that sapogenins are allied to the terpenes and that a more extended study of the crystalline sapogenins should be made on a larger scale. H. J. E.

2 : 6-Diaryl-4-methylpyrylium Salts and Pyranhydrones. WILHELM SCHNEIDER and FRITZ SEEBACH (*Ber.*, 1921, **54**, [*B*], 2285—2298).—In continuation of previous work (Schneider and Meyer, this vol., i, 680), it has now been found possible to isolate the pyrylium salts from the products of the reaction directly in the form of their sulphoacetates, thereby effecting a considerable improvement in the yields in certain cases. From aqueous solutions of the salts, it is possible by cautious addition of sodium hydroxide to precipitate the ψ-bases, but these pass into pyranhydrones when desiccated. The latter are, however, more conveniently obtained by the addition of concentrated sodium acetate solution to the sulphoacetates dissolved in water. Attempts to obtain the pyranhydrones in the crystalline condition have not yet been successful. The replacement of sodium acetate by weak organic bases, for example, aniline, phenylhydrazine, for the decomposition of


(I.)


(II.)

pyrylium salts leads unexpectedly to the production of pyridine derivatives. Thus, 2 : 6-diphenyl-4-methylpyrylium iodide and phenylhydrazine give 1-anilino-2 : 6-diphenyl-4-methylpyridinium iodide (I), which is converted by alkali into the anhydro-base (II). The latter class of substance has only been obtained up to the present from 4-methyl compounds.

The requisite sulphoacetic acid is prepared by cautious admixture of acetic anhydride (100 c.c.) and concentrated sulphuric acid (30 c.c.) and subsequent gentle heating of the mixture during two to three hours at a temperature which does not exceed 80°; at the end of this time free sulphuric acid is present only in traces.

Acetophenone is slowly converted by the mixture just described at 45—50° into 2 : 6-*diphenyl*-4-*methylpyrylium sulphoacetate*,

$$C_{18}H_{15}O\cdot SO_3\cdot CH_2\cdot CO_2H,$$

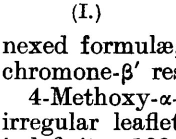
slender, yellow needles, m. p. 204°, from which the corresponding chloride, *bromide*, pale yellow needles, m. p. 194°, and *iodide*, long, red needles, m. p. 222°, are obtained; the latter salt is remarkable in that its solutions in dilute acid are pale yellow in colour and when cooled deposit the red salt without any previous darkening in shade. In a similar manner, but with a mixture containing a smaller proportion of sulphuric acid, anisole yields 2 : 6-*di*-p-*anisyl*-4-*methylpyrylium sulphoacetate*, $C_{20}H_{19}O_3\cdot SO_3\cdot CH_2\cdot CO_2H$, matt yellow needles, m. p. 198°. The corresponding *chloride*, $C_{20}H_{19}O_3Cl$, separates from alcoholic solution on the addition of ether as an orange-yellow, crystalline powder, m. p. 173°, from a mixture of alcohol and benzene in coarse, flesh-red *needles* ($+C_6H_6$) and slender, pale yellow *needles* ($+\frac{1}{2}C_6H_6$). The *bromide* forms slender, orange-yellow crystals, m. p. 193°, whereas the *iodide* is composed of slender, yellow needles or brown crystals, m. p. 204°. In this instance, the use of the sulphoacetate for the preparation of the corresponding pyranhydrone (cf. Schneider and Meyer, *loc. cit.*) is particularly advantageous.

1-*Anilino*-2 : 6-*diphenyl*-4-*methylpyridinium iodide*, a yellow, crystalline powder, m. p. 200°, is prepared by the addition of a solution of phenylhydrazine in benzene to a suspension of 2 : 6-diphenyl-4-methylpyrylium iodide in the boiling solvent. It is converted by a slight excess of very dilute aqueous sodium or potassium hydroxide solution into the *anhydro*-base (formula II above) dark blue needles, or hexagonal leaflets, m. p. 108°; it is somewhat unstable in solution in organic media. It is practically insoluble in water, in contact with which it behaves as a strong base which is able to displace ammonia from its salts. It readily re-forms the yellow quaternary pyridinium salts with acids and combines even with very weak acids, for example, carbonic. 2 : 4 : 6-*Triphenylpyrylium iodide*, a red, crystalline powder, m. p. 222°, is converted by phenylhydrazine in the presence of boiling benzene into the almost colourless 1-*anilino*-2 : 4 : 6-*triphenylpyridinium*

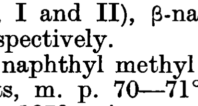
iodide, which does not give a coloured anhydro-base when heated in aqueous-alcoholic solution with dilute alkali hydroxide. H. W.

Production of Coumarins from Maleic and Malic Acids. G. C. Bailey and F. Boettner (*J. Ind. Eng. Chem.*, 1921, **13**, 905—906).—By heating together phenol and maleic acid in the presence of various dehydrating agents coumarin was not produced and with malic acid no appreciable quantities were formed. *m*-Cresol and malic acid in the presence of sulphuric acid produced methylcoumarin, a 50% yield on the weight of malic acid being obtained with a very pure *m*-cresol, and a 38—40% yield with an 80% *m*-cresol. Methylcoumarin is only one-tenth as toxic to white mice as coumarin. The perfume value of methylcoumarin is claimed to be equal to that of coumarin and its taste similar to, but slightly less intense than, that of the natural product. S. S. A.

Sulphoacetic Acid as Condensing Agent. III. Acetyl-naphthyl Methyl Ether and 3-Acetyl-2-methyl-β-naphthachromone-α. Wilhelm Schneider and Fritz Kunau (*Ber.*, 1921, **54**, [*B*], 2302—2310; cf. Schneider and Seebach, this vol., i, 877). α-Naphthyl methyl ether is transformed by an acetylating mixture prepared from acetic anhydride (70 c.c.) and concentrated sulphuric acid (10 c.c.) into 4-methoxy-α-naphthyl methyl ketone which has been obtained previously by Gattermann from α-naphthyl methyl ether, aluminium chloride, and acetyl chloride. Under similar conditions, β-naphthyl methyl ether is converted partly into 2-methoxy-α-naphthyl methyl ketone (cf. Fries, this vol., i, 424) (it is interesting to note that the Gattermann synthesis gives the isomeric 2-methoxy-β-naphthyl methyl ketone) and 3-acetyl-2-methyl-β-naphthachromone-α. The formation of the latter from 2-methoxy-α-naphthyl methyl ketone depends obviously on primary acetolysis of the methoxy-group by the sulphoacetic acid, internal condensation of 1-acetyl-β-naphthyl acetate with loss of water, and formation of the pyrone ring, and subsequent acetylation of the 2-methyl-β-naphthachromone-α in position 3.



(I.)



(II.)

It is proposed to term the isomeric β-naphthachromones (annexed formulæ, I and II), β-naphthachromone-α, and β-naphthachromone-β′ respectively.

4-Methoxy-α-naphthyl methyl ketone crystallises in pale yellow, irregular leaflets, m. p. 70—71° (*oxime,* colourless leaflets, m. p. indefinite, 122—127°, *picrate,* slender, red needles, m. p. 119—121°). The pyrylium derivative does not appear to be formed from α-naphthyl methyl ether and sulphoacetic acid. β-Naphthyl methyl ether likewise does not yield a pyrylium derivative, but is transformed into 2-methoxy-α-naphthyl methyl ketone, colourless needles, m. p. 56—57°, and 3-*acetyl-2-methyl-β-naphthachromone-α,* long, coarse, pale yellow needles, m. p. 157—158°. The latter is converted by hydroxylamine hydrochloride in boiling absolute

alcoholic solution in the presence of barium carbonate into a *substance*, pale brown needles, m. p. 250° (decomp.) (the amount was too small to allow of further investigation), the *dioxime*, $C_{16}H_{12}O(N\cdot OH)_2$, colourless needles, m. p. 201°, and *monoxime*, yellowish-white, irregular leaflets, m. p. 153°. 3-Acetyl-2-methyl-β-naphthachromone-α gives unstable additive *products* with bromine [m. p. 105—110° (decomp.)] and hydrogen chloride. It is converted by alcoholic ammonia into *2-methyl-β-naphthachromone-α*, pale yellow, irregular leaflets, m. p. 168°. The latter gives an unstable additive *compound*, m. p. 100° (decomp.), with bromine, an *oxime*, slender needles, m. p. 182°, and an *additive* compound, $C_{14}H_{13}O_2N$, yellow needles, m. p. 137°, with ammonia. 3-Acetyl-2-methyl-β-naphthachromone-α is converted by boiling dilute aqueous sodium hydroxide solution into β-naphthol and 2-hydroxy-α-naphthyl methyl ketone, m. p. 64° (cf. Fries, *loc. cit.*). H. W.

Derivatives of 3-Oxy(1)thionaphthen. SAMUEL SMILES and ERNEST WILSON MCCLELLAND (T., 1921, **119**, 1810—1816).

Carnitine. R. ENGELAND (*Ber.*, 1921, **54**, [*B*], 2208—2213).—Carnitine (A., 1905, i, 726; 1907, i, 264; 1908, i, 41, 842; 1909, i, 557) has been regarded by Fischer and Göddertz (A., 1911, i, 19) as identical with the hydroxybutyrobetaine, $O<\begin{matrix}NMe_3\text{—}CH_2\\CO\cdot CH(OH)\end{matrix}>CH_2$, but this view of its constitution is not readily reconcilable with the observation that it easily loses water when treated with concentrated sulphuric acid at about 130° (or by treatment with red phosphorus and concentrated hydriodic acid at 150—160°, or even at the boiling point of the mixture under atmospheric pressure) and yields *apo*carnitine. The compound prepared by Fischer and Göddertz, on the other hand, remains unchanged under these conditions and the non-identity of the two substances is further confirmed by the observation that *carnitine aurichloride* has m. p. 150—151° after softening at 145°, whereas the aurichloride of Fischer's compound melts at 166—171° (according to the rate of heating) after softening at 160—161°. Carnitine is more probably represented by the formula $O<\begin{matrix}NMe_3\cdot CH_2\\CO\text{—}CH\cdot CH_2\cdot OH\end{matrix}$, and its oxidation to β-homobetaine is explained by the instability of the intermediately formed "trimethylaminomethylmalonic acid," since it is found that positively-substituted malonic acids readily lose carbon dioxide even when heated in aqueous solution. The catalytic hydrogenation of *apo*carnitine to the corresponding saturated betaine can only be accomplished with some difficulty and uncertainty; the product formed (aurichloride, m. p. 172—173°) resembles most closely γ-butyrobetaine, but the identity of the two substances is not established with certainty, and, at present, it can only be stated that it differs decidedly from *α-n-* and *α-iso-*butyrobetaine and from β-*iso*butyrobetaine.

apo*Carnitine aurichloride*, $C_7H_{14}O_2N,AuCl_4$, crystallises in pale yellow, lustrous leaflets, m. p. 190—195° (decomp.), after softening

at about 180°; the corresponding *chloride* forms long, hygroscopic needles. Carnitine chloride is converted by concentrated sulphuric acid at 90—100° into carnitine ether, which was isolated in the form of its *aurichloride*, $C_{14}H_{30}O_5N_2,2AuCl_4$, m. p. (indefinite) 175—182° H. W.

Hygrine Alkaloids. IV. Di-1-methyl-2-pyrrolidylmethane. KURT HESS and FRANZ ANSELM (*Ber.*, 1921, **54**, [*B*], 2310—2326; cf. A., 1920, i, 497).—It has been shown previously that cuskhygrine is a derivative of di-1-methyl-2-pyrrolidylmethane; attempts to synthesise the latter are now recorded. This can be effected by the catalytic reduction of di-2-pyrryl ketone by hydrogen in the presence of platinum to di-2-pyrrolidylmethane (the course of the reaction is unusual and due to the presence of the carbonyl group, since the corresponding methylene compound is not reducible under these conditions) and methylation of the latter. The base is not homogeneous and can be separated into at least two biquaternary methylammonium iodides. Further examination of the base from cuskhygrine has disclosed the fact that it also is not uniform, and can be transformed into two well-defined biquaternary methylammonium iodides which are not identical with those obtained from the synthetic compound. The existence of these optically inactive isomerides appears to be explicable only on the assumption that the nitrogen atoms function as asymmetric centres and that di-1-methyl-2-pyrrolidylmethane resembles stereochemically the saccharic acids and exists in six optically inactive forms, two of which belong to the non-resolvable meso-type. In favour of this conception, the isolation of a possible fifth isomeride is recorded.

Di-2-pyrryl ketone, m. p. 156—157°, is conveniently prepared by passing a current of carbonyl chloride into an ethereal solution of magnesium pyrryl bromide. It gives a *hydrazone*, m. p. 115—117°, which is converted by sodium ethoxide at 150° into di-2-pyrrylmethane, b. p. 163—167°/12 mm., m. p. 73° [Pictet and Rilliet (A., 1907, i, 445) give m. p. 66°]. The ketone is reduced by hydrogen in the presence of platinum (the apparatus is fully described and depicted in the original) to a mixture of di-2-pyrrolidylmethanes, b. p. 112—122°/15 mm., which is converted by formaldehyde and formic acid into a mixture of di-1-methyl-2-pyrrolidylmethanes, b. p. 115—120°/15 mm. The latter, when treated with methyl iodide, gives two crystalline *biquaternary methiodides*, needles, m. p. 180°, and four-sided platelets, m. p. 290° (incipient decomp.) [corresponding *aurichloride*,

$$C_{13}H_{28}N_2Au_2Cl_8,$$

yellow, microcrystalline precipitate, m. p. about 275° (decomp)], whilst apparently a third *isomeride*, cubes or prisms, m. p. 146—147°, was isolated in quantity too small to permit of analysis. The base from cuskhygrine is similarly convertible into two biquaternary methiodides, m. p. 263° and 201° respectively, the latter of which has been described previously by Hess and Fink (A., 1920, i, 497).

The action of hydrazine hydrate on cuskhygrine (Hess and Fink, *loc. cit.*) has been further investigated, and it is now found that in the presence of a little water cuskhygrine-α-hydrazone, b. p. 182—185°/11 mm., and relatively much smaller amounts of *hygrine-hydrazone*, b. p. 125—130°/11 mm., are produced. The latter is hydrolysed readily by dilute sulphuric acid to hygrine, and is converted by sodium ethoxide solution at 150° into α-1-methyl-2-pyrrolidylpropane, b. p. 140—142° (cf. A., 1914, i, 199). The isomerism of the cuskhygrine-α- and -β-hydrazones remains unexplained, but it is shown that the former regenerates cuskhygrine smoothly under the influence of acids.

The transformation of cuskhygrine into hygrine by alkalis has been recorded previously; the change can also be produced by hydrochloric acid at 170—180°.

Attempts to oxidise 1-methyl-2-pyrrolidylacetic acid to 1-methylpyrrolidine-2-carboxylic acid were unsuccessful by reason of the unexpected stability of the original material. H. W.

Constitution of Matrine. I. HEIZABURÔ KONDÔ and SHINICHI SATÔ (*J. Pharm. Soc. Japan*, 1921, 659—679).—*Matrine*, $C_{15}H_{24}ON_2$, is one of the principal alkaloids of the roots of *Sophora flavescens*, Ait. (*S. angustifolia*, S. and Z.) and is a monoacidic tertiary amine. Of the two nitrogen atoms, one forms a lactam ring with a carboxyl group and is changed to an imino-group by hydrolysis with alkali, *matrinic acid* being formed (*ibid.*, 1889, No. 84; 1903, Nos. 260—262). Matrine hydrochloride was mixed thoroughly with fourteen times its weight of zinc dust and distilled in a combustion tube, the distillate being absorbed in dilute hydrochloric acid. The distillate was made alkaline, and subjected to steam distillation. The residue consisted mainly of matrinic acid mixed with a black resin; the colourless oil of peculiar odour which distilled was acidified with hydrochloric acid and precipitated with mercuric chloride, the mercury was removed by means of hydrogen sulphide, and the two admixed bases were separated by distillation under reduced pressure.

The *base*, $C_{10}H_9N$, distilled at 87°/19 mm. or 188—189°/760 mm., and gave the following derivatives: *Hydrochloride*, deliquescent, long needles; *mercurichloride*, white prisms, m. p. 206°; *picrate*, yellow prisms, m. p. 165°; *aurichloride*, yellow lamellæ, m. p. 143—144°; *platinichloride*, long lamellæ, decomposing at 216—217°; *methiodide*, m. p. 241°. From the methiodide the corresponding *ammonium chloride* was prepared as deliquescent, colourless needles; this gave a *mercurichloride*, m. p. 216°; *picrate*, yellow needles, m. p. 211°; *platinichloride*, octahedra, m. p. 223—224° (decomp.); and *aurichloride*, yellow needles, m. p. 239—240°. The *methylammonium hydroxide* of the base, a brown syrup, shows the characteristic behaviour of a base of this class, and on distillation with potassium hydroxide yields methyl alcohol, the original base, and some products of decomposition.

The second base, *matridine*, $C_{15}H_{26}N_2$, white needles, m. p. 76°, does not distil at 160°/19 mm., and is a reduction product of matrine,

the carboxyl group having been changed into the CH_2-group. Its properties resemble those of matrine, but it does not yield matrinic acid when hydrolysed. The *hydrochloride*, $C_{15}H_{26}N_2,2HCl$, long, white needles, sublimes without melting; the *aurichloride*, forms yellow lamellæ, m. p. 216°. K. K.

Strychnos Alkaloids. XXIX. Oxidation of Cryptobrucinolone and its Preparation from Brucinolone-*b*. HERMANN LEUCHS, EMIL HELLRIEGEL, and HARRY HEERING (*Ber.*, 1921, **54**, [*B*], 2177—2190).—The crude mixture of *a*- and *b*-acetylbrucinolone is converted by methyl alcoholic ammonia at 100° into the pure *b*-form; attempts to effect this transformation more conveniently by the use of ethyl-alcoholic potassium hydroxide solution resulted in the preparation of a mixture of ethoxydihydrobrucinolone and cryptobrucinolone (Leuchs and Pierce, A., 1912, i, 898), thus giving a convenient method of obtaining the latter which has now been subjected to prolonged examination. It is remarkable that in the series: brucinolone-*a* $\xrightarrow[\text{cold alkali}]{\text{NH}_3}$ brucinolone-*b* $\xrightarrow[\text{alkali}]{\text{hot alcoholic}}$ cryptobrucinolone, a double bond appears first to be displaced further from the nitrogen atom by one carbon atom and then, under similar conditions, to resume its previous position; thus probably indicating further changes in the remainder of the molecule under the influence of alcoholic potassium hydroxide solution. The change does not, however, appear to affect the aromatic residue of the brucine molecule, since it has the same reactions in cryptobrucinolone as in the other brucinolones.

Ethoxydihydrobrucinolone, $C_{23}H_{28}O_6N_2$, colourless, lustrous prisms (+1MeOH), m. p. generally about 110°, but occasionally about 132° after softening at 106°, $[\alpha]_D^{20}$ −44·2° in glacial acetic acid solution; pointed prisms (+1EtOH), m. p. 135° (decomp.) after softening at 130°; anhydrous, m. p. 105—125°, $[\alpha]_D^{20}$ −44·0°, and cryptobrucinolone, pale greenish-yellow leaflets, m. p. 190—192°, $[\alpha]_D^{17}$ −150·9° when dissolved in glacial acetic acid, are prepared by the action of hot alcoholic potassium hydroxide solution on pure or crude acetylbrucinolone-*b*; in addition, there is isolated a *substance* which is soluble in alkali hydroxide and is termed *hydroxydihydrobrucinolone-III*, $C_{21}H_{24}O_6N_2$, colourless leaflets or slender needles, m. p. 219—221° after softening at 213°, $[\alpha]_D^{17}$ −49·5° in glacial acetic acid solution. The ethoxydihydro-compound is converted by alcoholic potassium hydroxide solution into cryptobrucinolone, whereas the latter is unaffected. *Ethoxydihydrobrucinolone acetate* forms colourless prisms, m. p. 219—220°, $[\alpha]_D^{16}$ −78·2° in glacial acetic acid solution. Cryptobrucinolone is converted by 5*N*-nitric acid at 0° into the corresponding *quinone*, $C_{19}H_{16}O_5N_2$, lustrous, red needles, which become discoloured above 250°; the latter is reduced by sulphurous acid to the *quinol*, $C_{19}H_{18}O_5N_2$, which is amorphous. Similarly, 14*N*-nitric acid at 0° transforms cryptobrucinolone into the *nitroquinone*, $C_{19}H_{15}O_7N_3$, orange-coloured needles, which is reduced to the *nitroquinol*,

$C_{19}H_{17}O_7N_3$, ochre-yellow, rectangular prisms, decomp. 263—265°. *Acetylcryptobrucinolone*, short, prismatic rods, m. p. 272—274°, $[\alpha]_D^{15}$ −199·5° in glacial acetic acid solution, is prepared with the aid of sodium acetate and acetic anhydride; it is oxidised by potassium permanganate in acetone solution to an *acid*, $C_{23}H_{24}O_{10}N_2,0·5H_2O$, slender, colourless needles, m. p. about 280° (slight decomp.), which is most definitely characterised by its *copper* salt, $C_{23}H_{22}O_{10}N_2Cu,8H_2O$, apple-green needles and prisms and *ferric* salt, $(C_{23}H_{23}O_{10}N_2)_2Fe·OH$, brownish-violet prisms or needles. The acid is decomposed by 12*N*-hydrochloric acid at 100° into oxalic and acetic acids and non-crystalline basic products; it must therefore contain the groups :N·CO·CO_2H and CO_2H·C⋮ formed from the arrangement :N·CO·CH:CH·C⋮. Cryptobrucinolone is oxidised by permanganate in acetone solution to a *substance* crystallising in slender needles, m. p. 260° (decomp.) after softening at 230°, which dissolves in a large excess of alkali hydroxide solution.

Acetoxydihydrobrucinolone-I forms short, thick prisms, m. p. 253—254°, $[\alpha]_D^{15}$ −22·3° in glacial acetic acid solution. When cryptobrucinolone is heated with acetic anhydride at 100° (in the absence of sodium acetate) it is converted into a mixture of the corresponding acetate and dehydrobrucinolone acetate [brucinolone acetate-*c*], yellow needles or prisms, m. p. 312°, $[\alpha]_D^{18}$ −431° in glacial acetic acid solution, which is identical with the product obtained by the oxidation of acetylbrucinolone-*b* in acetone solution (A., 1912, i, 210). When heated with methyl-alcoholic ammonia at 100° it gives (?) *dehydrobrucinolone*, yellow, rectangular platelets, m. p. about 315° (decomp.), $[\alpha]_D^{20}$ −376° in glacial acetic acid solution, from which the acetate is readily re-formed. Brucinolone-*b* appears to be partly converted by acetic anhydride at 100° into dehydrobrucinolone acetate. H. W.

Acid Methylarsenate of Strychnine. J. Bouillot (*J. Pharm. Chim.*, 1921, [vii], **24**, 289—294).—Conflicting statements have appeared at various times regarding the composition and properties of strychnine methylarsenate, but it is now definitely shown that the strychnine methylarsenate of commerce is actually the acid salt of the composition $AsMeO(OH)_2,C_{21}H_{22}O_2N_2,2H_2O$. This salt is prepared by dissolving in hot aqueous alcohol equimolecular proportions of methylarsenic acid and strychnine, and allowing to crystallise by spontaneous evaporation, preferably in presence of sulphuric acid in a vacuum. Colourless needles are thus obtained, soluble in 14·5 parts of water at 20°, and in 146 parts of 90% alcohol. In 5% aqueous solution α_D −21°. The salt is stable at ordinary temperatures, but commences to decompose at temperatures above 60°. G. F. M.

Phenacyl- and Dihydroxyphenacyl-derivatives of Theobromine and Theophylline, and their corresponding Secondary Alcohols. C. Mannich and S. Kroll (*Ber. deut. Pharm. Ges.*, 1921, **31**, 291—310).—With the object of preparing new

caffeine derivatives in which the stimulating action of caffeine on the nerve system was eliminated whilst the cardiac action was retained, substances were prepared in which the phenacyl radicle, $COPh{\cdot}CH_2-$, and the group, $C_6H_3(OH)_2{\cdot}CH(OH){\cdot}CH_2-$, characteristic of adrenaline, were introduced into the xanthine molecule. The desired physiological result was not obtained, however, phenacyltheobromine and phenacyltheophylline showing no advantage over theophylline, and the adrenaline–caffeine derivatives being physiologically inactive. The preparation and properties of the following are described: 7-*Phenacyltheophylline*,

$$\begin{array}{l} NMe{\cdot}CO{\cdot}C\text{——}N{\cdot}CH_2{\cdot}COPh, \\ CO{\cdot}NMe{\cdot}C{\cdot}N{:}CH \end{array}$$

prepared by the action of ω-bromoacetophenone on sodium theophylline, forms white, silky needles, m. p. 188°. It yields an *oxime*, m. p. 233°, and a *semicarbazone*, m. p. 225°. When reduced with palladium and hydrogen, it gives the corresponding secondary alcohol, α-*phenyl*-β-*theophyllinoethanol*, $C_5N_4HO_2Me_2{\cdot}CH_2{\cdot}CHPh{\cdot}OH$, m. p. 159°.

3 : 4-*Dimethoxy*-7-*phenacyltheophylline*, prepared by condensing sodium theophylline with ω-bromoacetoveratrone, forms white needles, m. p. 212°, and gives an *oxime*, m. p. 216°. On reduction with palladium and hydrogen, it gives the corresponding secondary alcohol, α-3 : 4-*dimethoxyphenyl*-β-*theophyllinoethanol*, m. p. 181°. On attempting to demethylate this with hydriodic acid decomposition ensued.

3 : 4-*Dihydroxyphenacyltheophylline* was obtained by demethylating the above compound with hydriodic acid; it gives a green coloration with ferric chloride, turning to red with ammonia (catechol reaction). Its *diacetyl* derivative melts at 203°. On reduction with palladium and hydrogen followed by hydrolysis it is converted into the corresponding secondary alcohol, α-3 : 4-*dihydroxyphenyl*-β-*theophyllinoethanol*, which may be regarded as a derivative of adrenaline on the one hand and of caffeine on the other. The substance forms a grey, crystalline powder, which decomposes towards 220° without melting. Its *triacetyl* derivative forms white needles, m. p. 114°. 1-*Phenacyltheobromine*, prepared similarly to the corresponding theophylline derivative, melts at 171°, and gives an *oxime*, m. p. 215°, and a semicarbazone, m. p. 215—216°. The corresponding secondary alcohol, α-*phenyl*-β-*theobrominoethanol*, forms white needles, m. p. 110°, with loss of 1 mol. of water of crystallisation. The anhydrous substance then melts at 147°.

3 : 4-*Dimethoxyphenacyltheobromine*, prepared in similar manner to the theophylline derivative, forms silky crystals, m. p. 227°, and gives the corresponding secondary *alcohol*, m. p. 195°, on reduction with aluminium amalgam in dilute alcoholic solution. Demethylation with hydriodic acid of the methoxyphenacyltheobromine gave grey needles of 3 : 4-*dihydroxyphenacyltheobromine*, decomposing at 280° without melting. Its *diacetyl* derivative, m. p. 208°, on reduction with aluminium amalgam in alcoholic solution, followed by hydrolysis with alcoholic potassium hydroxide in absence of air, gives α-3 : 4-*dihydroxyphenyl*-β-*theobrominoethanol*,

forming a grey, crystalline powder decomposing at 170° without melting. It gives a white, crystalline *triacetate*, m. p. 147°.

G. F. M.

***d*-Lupanine, $C_{15}H_{24}ON_2$.** GÖSTA MOLANDER (*Ber. deut. Pharm. Ges.*, 1921, **31**, 265—270).—Contrary to the statements of Beckel (A., 1911, i, 743; 1913, i, 86), the action of alcoholic bromine on lupanine hydrochloride does not result in a decomposition into two new bases, but gives a brominated compound of the composition $C_{15}H_{24}ON_2,HBr,Br_2$ or $C_{15}H_{22}Br_2ON_2,HBr$ in yellow crystals, from which bromine is readily eliminated by boiling with alcohol, with the formation of colourless crystals of lupanine hydrobromide, m. p. 240°. *d*-Lupanine is very resistant also to the action of fuming hydrochloric acid under pressure, and to 50% potassium hydroxide. It yields a syrupy base having a crystalline hydrochloride, m. p. 158°, when boiled with 40% alcoholic potassium hydroxide.

G. F. M.

Crystallographic Descriptions of some Pyridine and Picoline Derivatives. MARY WINEARLS PORTER (T., 1921, **119**, 1769—1773).

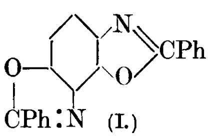
Derivatives of Tetrahydrocarbazole. WILLIAM HENRY PERKIN, JUN., and SYDNEY GLENN PRESTON PLANT (T., 1921, **119**, 1825—1839).

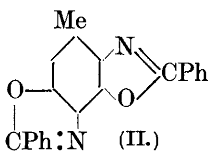
Relation between Fluorescence and Chemical Constitution in Benzoxazole Derivatives. F. HENRICH (*Ber.*, 1921, **54**, [*B*], 2492—2511).—The author has shown that 5-hydroxy-1-phenyl-3-methylbenzoxazole exhibits green fluorescence in various solvents even after purification by repeated crystallisation (A., 1897, i, 446; 1899, i, 171). This compound and other benzoxazole derivatives have recently been prepared by Skraup (A., 1919, i, 598), who states that they lose their fluorescent properties when repeatedly purified by crystallisation from solutions treated with animal charcoal. The author has again prepared this compound and subjected it to repeated fractional crystallisation, treatment with animal charcoal, dissolution in alkali hydroxide solution, and reprecipitation, etc., the fluorescence remaining undiminished.

A number of oxazole derivatives have been prepared and examined to ascertain which of them exhibit to the unassisted eye fluorescence in solution. A distinction must be drawn between fluorescence shown in aqueous alkali solution and organic solvents, especially alcohol, and that shown in concentrated sulphuric acid solutions, which fluoresce the most readily. In order to convert benzoxazole into substitution products fluorescing visibly in solution, the first essential is for the μ-[1]-position to be occupied by an aromatic residue. The three 5-hydroxy-derivatives of the form $OH\cdot C_6H_3{<}^{N}_{O}{>}C\cdot C_6H_4Me$ fluoresce strongly, whereas the corresponding compound with benzyl in place of tolyl shows no fluorescence even if the 3-position is occupied by a methyl group. The presence in position 5 of a salt-forming group, preferably hydroxyl,

intensifies the fluorescent properties: thus, 3-hydroxy-1-phenyl-, 4-hydroxy-1-phenyl-, and 6-hydroxy-1-phenyl-benzoxazoles do not, whereas 5-hydroxy-1-phenylbenzoxazole does show fluorescence in alkali solution; in the latter case, introduction of methyl in the 3-position enhances the fluorescence, but 3-hydroxy-1-phenyl-5-methylbenzoxazole is non-fluorescent.

Replacement of the hydroxylic hydrogen of 5-hydroxy-1-arylbenzoxazoles by methyl or ethyl gives a compound of distinct but weakened fluorescence in sulphuric acid or alcohol, and replacement of this hydrogen by acid residues produces increased weakening; further replacement in the 3-, 4-, and 6-positions usually annuls the fluorescence. With reference to Meyer's theory of the relationship between fluorescence and chemical constitution (A., 1898, ii, 105, 275), it is found that the compounds I and II, prepared by distilling benzoyl chloride with diamino-resorcinol and -orcinol respectively, are almost devoid of fluorescence, even in concentrated sulphuric acid solution.


(I.)


(II.)

Noteworthy is the occurrence of fluorescence in sulphuric acid with compounds in which the 5-position is occupied by a methyl group. Thus, 1-phenyl-5-methylbenzoxazole and 1-*o*-, 1-*m*-, and 1-*p*-tolyl-5-methylbenzoxazoles, prepared from the reduction product of the volatile mononitro-*m*-cresol, exhibit comparatively strong fluorescence in concentrated sulphuric acid.

[With Gust. Opfermann.]—3-*Acetoxy*-1-*methylbenzoxazole*, $C_{10}H_9O_3N$, prepared from *o*-aminoresorcinol hydrochloride and acetic anhydride, forms dense, white crystals, m. p. 68°, and shows no fluorescence in organic solvents, concentrated sulphuric acid, or potassium hydroxide solution.

3-*Benzoyloxy*-1-*phenylbenzoxazole*, $C_{20}H_{13}O_3N$, obtained by the action of benzoyl chloride on *o*-aminoresorcinol hydrochloride, forms nodular masses of needles, m. p. 143—144° with previous sintering, and yields 3-hydroxy-1-phenylbenzoxazole (Henrich and Opfermann, A., 1904, i, 934) on hydrolysis.

3-*Hydroxy*-1-*benzylbenzoxazole*, $C_{14}H_{11}O_2N$, prepared from phenylacetyl chloride and *o*-aminoresorcinol hydrochloride, forms crystals, m. p. 185°, but does not give fluorescent solutions.

5-*Hydroxy*-1-*benzylbenzoxazole*, $C_{14}H_{11}O_2N$, prepared from phenylacetyl chloride and *as*-aminoresorcinol, crystallises in white, nodular masses, m. p. 154°; its solution in alkali does not fluoresce.

5-*Hydroxy*-1-o-*tolylbenzoxazole*, $C_{14}H_{11}O_2N$, from *o*-toluoyl chloride and *as*-aminoresorcinol, forms crystals, m. p. 135°, and gives a pronounced green fluorescence when dissolved in alkali solution.

5-*Hydroxy*-1-p-*tolylbenzoxazole* forms crystals, m. p. 236·5°, and shows green fluorescence in alkali solution.

5-*Hydroxy*-1-*benzyl*-3-*methylbenzoxazole*, $C_{15}H_{13}O_2N$, forms crystals, m. p. 149°; its solution in dilute alkali hydroxide shows no fluorescence.

[With K. ROEDEL.]—6-*Benzoylamino*-5-*benzoyloxy*-1-*phenylbenzoxazole*, $C_{27}H_{18}O_4N_2$, prepared by the action of benzoyl chloride on the hydrochloride of diaminoresorcinol obtained by reducing dinitrosoresorcinol (Fitz, *Ber.*, 1875, **8**, 633), separates in crystals, m. p. 283°, and, when subjected to dry distillation, yields as-1 : 1′-*diphenylbenzdioxazole* (formula I, above), which forms pale yellow crystals, m. p. 192°, and exhibits pale blue fluorescence in concentrated sulphuric acid.

as-1 : 1′-*Dimethylbenzdioxazole*, $C_{10}H_8O_2N_2$, obtained from acetic anhydride and diaminoresorcinol hydrochloride, gives crystals, m. p. 192°, and is devoid of fluorescent properties in sulphuric acid.

[With F. ROSSTEUTSCHER.]—*Hexa-acetyldiamino-orcinol*,

$C_{19}H_{22}O_8N_2$,

prepared by the action of acetic anhydride on diamino-orcinol hydrochloride, forms white crystals, m. p. 137—138°, and, when distilled in absence of solvent, yields as-1 : 1′ : 4-*trimethylbenzdioxazole*, $C_{11}H_{10}O_2N_2$, which forms crystals, m. p. 140—141°, dissolves readily in cold concentrated sulphuric acid to a non-fluorescent solution, and forms a *bromo*-derivative, small needles, m. p. 233°.

[With F. ROSSTEUTSCHER and N. MATULKA.]—*Benzoylaminobenzoyloxy*-1-*phenylmethyloxazole*, $OBz \cdot C_6HMe(NHBz){<}{}^{O}_{N}{>}CPh$, prepared from benzoyl chloride and diamino-orcinol hydrochloride, forms colourless crystals, m. p. 246—247°, yields scarcely fluorescent solutions in alkali hydroxide solution and in sulphuric acid, and, when hydrolysed, gives *hydroxybenzoylamino*-1-*phenylmethyloxazole*, $C_{21}H_{16}O_3N_2$, which forms crystals, m. p. 234—235°; by alcoholic potassium hydroxide either of these compounds is apparently converted into the compound, $OH \cdot C_6HMe(NH_2){<}{}^{O}_{N}{>}CPh$, which was not obtained in sufficient quantity for analysis. When subjected to dry distillation, benzoylaminobenzoyloxy-1-phenylmethyloxazole yields the *compound*, $C_{21}H_{14}O_2N_2$ (formula II, above), which crystallises in yellow needles, m. p. 189—190°, and gives a faintly fluorescing solution in sulphuric acid.

[With K. ROEDEL.]—*Aminoquinol*, $C_6H_7O_2N$, prepared by the reduction of nitroquinol (Elbs, A., 1893, i, 640), was separated as *hydrochloride*. By benzoylation and ortho-condensation, it is converted into 4-*benzoyloxy*-1-*phenylbenzoxazole*, $C_{20}H_{13}O_3N$, which forms white crystals, m. p. 154·5°, and in sulphuric acid shows slight fluorescence; on hydrolysis it yields 4-*hydroxy*-1-*phenylbenzoxazole*, $C_{13}H_9O_2N$, crystallising in white needles, m. p. 175°, and showing a faint blue fluorescence in concentrated sulphuric acid.

[With W. WUNDER.]—3-*Aminocatechol hydrochloride*,

$C_6H_7O_2N,HCl$,

prepared by reduction of the nitrocatechol volatile in steam (cf. Weselsky and Benedikt, A., 1882, 1200), gives a dark green coloration with ferric chloride, a pale coloration with hypochlorite solution and hydrochloric acid, and a brownish-yellow coloration with potassium dichromate and sulphuric acid. Treatment with

benzoyl chloride converts it into 6-*benzoyloxy*-1-*phenylbenzoxazole*, which distils at above 400°; 6-*hydroxy*-1-*phenylbenzoxazole*, $C_{13}H_9O_2N$, forms snow-white needles, m. p. 191—192°, and shows slight fluorescence in sulphuric acid, but not in sodium hydroxide solution.

[With N. MATULKA.]—4-*Amino*-m-*cresol* [CH_3 : OH : NH_2= 1 : 3 : 4] *hydrochloride* (cf. von Auwers, Borsche, and Weller, this vol., i, 571) reacts (1) with benzoyl chloride, giving 1-*phenyl*-5-*methylbenzoxazole*, $C_{14}H_{11}ON$, white needles, m. p. 92·5°, which gives a highly fluorescent solution in concentrated sulphuric acid; (2) with *o*-toluoyl chloride, giving 1-o-*tolyl*-5-*methylbenzoxazole*, $C_{15}H_{13}ON$, which crystallises in slender, white needles with a faint odour, m. p. 94—95°, and forms a non-fluorescent alcoholic solution, but in concentrated sulphuric acid shows bluish-violet fluorescence; (3) with *m*-toluoyl chloride, giving 1-m-*tolyl*-5-*methylbenzoxazole*, colourless needles, m. p. 87°, the alcoholic solution of which shows no, and the sulphuric acid solution blue, fluorescence; (4) with *p*-toluoyl chloride, giving 1-p-*tolyl*-5-*methylbenzoxazole*, m. p. 117—118°, the sulphuric acid solution of which shows slight blue fluorescence. T. H. P.

The Constitution of the Polysulphonated Derivatives of Indigotin. E. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 586—587; cf. A., 1910, i, 74).—Indigotintetrasulphonic acid (Juillard, A., 1893, i, 348) on oxidation gives an isatindisulphonic acid in the form of its potassium salt, which when acted on by bromine in concentrated solution yields 5 : 7-dibromoisatin. Thus the original acid must have been indigotin-5 : 7 : 5′ : 7′-tetrasulphonic acid. W. G.

The Mechanism of Oxidative Processes. IV. HEINRICH WIELAND (*Ber.*, 1921, **54**, [*B*], 2353—2376).—The communication deals with (i) the oxidative decolorisation of indigotin, (ii) the oxidation of aldehydes, (iii) the catalytic decomposition of hydrogen peroxide, (iv) the peroxides as hydrogen acceptors, and (v) the biological significance of catalases.

(i) In a series of communications (A., 1913, i, 1304; 1914, i, 1007), the hypothesis has been advanced that the catalytic action of finely-divided metals in promoting oxidation is not due to activation of the oxygen, but of the hydrogen of the substrate; the process is therefore one of dehydrogenation and not of oxidation, the oxygen serving merely as acceptor for the activated hydrogen. The most marked apparent exception to this conception is the decolorisation of indigotindisulphonic acid. In extension of the observations of Kalb (A., 1910, i, 340; 1911, i, 680), however, it is now shown that indigotinsulphonic acid is converted into its dehydro-derivative by palladium black and air (the process can be arrested at this stage in pyridine, but not in aqueous solution) and that dehydroindigodatinsulphonic acid is hydrolysed to isatinsulphonic acid and indigotindisulphonic acid under the experimental conditions adopted. The catalytic decolorisation of indigotin is therefore to be regarded as a case of dehydrogenation.

(ii) Further examination of the autoxidation of aldehydes has proved that the process is catalytically accelerated by animal charcoal to almost the same extent as by palladium black. Under all conditions, dry acetaldehyde absorbs oxygen to form mainly peracetic acid, whereas only acetic acid is obtained with moist acetaldehyde, pointing thus to the conclusion that it is the aldehyde hydrate which is dehydrogenated by the per-acid, $CHMe(OH)_2 + Me{\cdot}C(:O){\cdot}O{\cdot}OH = 2Me{\cdot}CO_2H + H_2O$. With benzaldehyde, on the other hand, much benzoic acid is formed even when every precaution to exclude moisture is observed and the process may be interpreted as follows, $Ph{\cdot}CHO + PhC(:O){\cdot}O{\cdot}OH \longrightarrow PhCH(OH){\cdot}O{\cdot}O{\cdot}C(:O){\cdot}Ph \longrightarrow 2Ph{\cdot}CO_2H$. The rate of autoxidation of salicylaldehyde is very small and is not markedly increased by the catalysts used; chloral and chloral hydrate, unfortunately, cannot be oxidised catalytically.

(iii) The decomposition of hydrogen peroxide has been shown repeatedly to be an action of the first order. According to the author's conception, however, it consists of two phases, the dehydrogenation of the first molecule which is actually observed and the immeasurably rapid reductive fission of the second molecule. $HO{\cdot}OH \longrightarrow O:O + 2H$ and $HO{\cdot}OH + 2H \longrightarrow 2H_2O$. The whole reaction is precisely analogous to the decomposition of hydrazobenzene at its melting point, or at the atmospheric temperature in the presence of palladium black. Evidence in favour of this view is obtained by allowing the reaction to proceed in the presence of more potent hydrogen acceptors than hydrogen peroxide itself. Suitable substances are potassium persulphate in the presence of palladium black or animal charcoal, but not of blood-catalase, benzoyl peroxide which suffers reduction to benzoic acid in ethereal solution, dehydroindigotin, which is reduced to indigotin in pyridine solution by ethereal hydrogen peroxide in the presence of palladium black, and sodium nitrosodisulphonate, which is reduced to sodium hydroxylaminedisulphonate in the presence of palladium black. Blood catalase and yeast catalase are inactive towards dehydroindigotin and sodium nitrosodisulphonate.

(iv) Hydrogen peroxide can behave as a hydrogenating agent by loss of hydrogen and liberation of molecular oxygen, as a dehydrogenating agent by reacting with hydrogen and, in many reactions, as a true oxidising agent. The di-secondary peroxides can exhibit only the second type of action. It is shown in the case of potassium persulphate, dibenzoyl peroxide, and diethyl peroxide that they can behave as acceptors in catalytically accelerated dehydrogenations, quinol being used as substrate. The powerful catalytic action of animal charcoal in the reactions with persulphate and benzoyl peroxide is remarkable; there can be no doubt that in this case, as with palladium black, the adsorbed quinol suffers a change in its structure which is manifested by the less firm union of its hydrogen atoms. Blood catalase also greatly accelerates the dehydrogenation of quinol by potassium persulphate. Acetaldehyde and potassium persulphate do not react with one

another in 1% solution; the dehydrogenation of the aldehyde-hydrate is, however, with persulphate as acceptor, accelerated by palladium black, as is also that of dextrose.

(v) The processes which consume oxygen and occur in the living cell are not to be explained by enzymatic activation of molecular oxygen but by activation of the hydrogen in the substance which suffers combustion. The hypothesis is supported by evidence drawn from the work of Thunberg (A., 1920, i, 784), Lipschitz (this vol., i, 203), and Batelli and Stern (*Chem. Zentr.*, 1921, i, 581).

H. W.

The Constitution of Isatin Salts and Isatol. GUSTAV HELLER (*Ber.*, 1921, **54**, [*B*], 2214—2222).—A reply to the recent criticism of Hantzsch (this vol., i, 597) on the author's work in the isatin series.

It is pointed out that Hantzsch's view of the non-existence of isatin *N*-salts is mainly supported by arguments based on the behaviour of ethyl acetoacetate and similar tautomeric substances. The comparison is, however, scarcely valid, since, in general, such isomerism in cyclic systems leads to the development of phenolic character and consequently of acidic properties in the lactim form, —N:C(OH)—. In the ring system of isatin lactim, however, the hydroxyl under the influence of the nitrogen atom has no actual phenolic character, but behaves more nearly as a tertiary alcoholic group which is susceptible of alkylation to a readily-hydrolysed ether, but does not allow the replacement of the hydrogen atom by alkali.

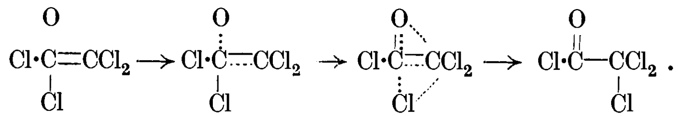
With regard to practical details, the production of isatol from isatin silver and benzoyl chloride is again confirmed, and the uniformity of the product is established by crystallographic measurements. Contrary to Hantzsch's assumption, a comparison of the physical and chemical properties of isatol and methylisatoid of von Baeyer and Ökonomides shows that these substances are not identical. Hantzsch's statement that methylisatoid does not contain the methyl group since it can also be prepared from isatin silver and ethyl iodide is not supported by the author's experiments, since he finds the ethylisatoid thus formed to differ from methylisatoid.

H. W.

Explanation of certain Transformations of Oxonic Acid and of Allantoxaidin. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1921, **54**, [*B*], 2441—2448).—Oxonic acid, the identity of which with allantoxanic acid was demonstrated by the authors (A., 1920, i, 885), and also allantoxaidin may be readily converted into cyanuric acid and into biuret. The yields are good, but it is not easy to explain by simple reactions the opening of the 4 : 5-carbon–carbon linking, as similar linkings in other analogous compounds show great stability. The following results furnish the explanation required.

The oxidations of oxonic acid and allantoxaidin to cyanuric acid by acid permanganate solution or other oxidising agent are examples of oxidation rearrangements (Biltz, A., 1913, i, 241)

analogous to the oxidation of bisdiphenylene-ethylene to diphenyl-phenanthrene (Klinger and Lonnes, A., 1896, i, 691). The similar oxidation of tetrachloroethylene to trichloroacetyl chloride (Biltz, A., 1902, i, 417) may be represented thus :



According to this view, allantoxaidin should exhibit combining power at the carbon–nitrogen pair united by a double linking. It is, indeed, found that allantoxaidin unites with sodium hypobromite, the bromine atom passing to the 6-nitrogen atom and the ONa group to the 5-carbon atom. By the action of acetic acid on the resulting compound, the sodium may be replaced by a hydrogen atom, giving 5-bromoamino-5-hydroxyhydantoin. The latter, and also its sodium derivative, undergoes even in the cold, although more rapidly on heating, a species of Hofmann's reaction, with formation of cyanuric acid :

$$CO<\begin{array}{l}NH\cdot C(ONa)\cdot NHBr\\ NH\cdot CO\end{array} \longrightarrow \left[CO<\begin{array}{l}NH\cdot CBr(ONa)\\ NH\text{———}CO\end{array}>NH\right] \longrightarrow$$
$$CO<\begin{array}{l}NH\cdot CO\\ NH\cdot CO\end{array}>NH\,;$$

the intermediate product assumed cannot, however, be isolated. The transformation of *cyclo*pentanonoxime into α-piperidone, that of oximinocamphor into camphorimide, and many other similar ring-enlargements are known. This formation of cyanuric acid from allantoxaidin furnishes support for Ponomareff's formula for allantoxaidin (A., 1879, 227, 461) the reaction being inexplicable on the basis of the constitution $CO<\begin{array}{l}N{=}C\cdot NH_2\\ NH\cdot CO\end{array}$.

The decomposition of allantoxaidin into biuret and formic acid when heated in aqueous solution, either alone or with acid, may be explained if it is assumed that the molecule of water of crystallisation is combined by the allantoxaidin with formation of 5-amino-5-hydroxyhydantoin. The latter contains hydroxyl and carbonylic oxygen at two adjacent carbon atoms, and, like many analogous compounds, such as lactic acid, which decomposes into acetaldehyde and formic acid, shows a tendency to undergo fission :

$$CO<\begin{array}{l}NH\cdot C(OH)\cdot NH_2\\ NH\cdot CO\end{array} \longrightarrow CO<\begin{array}{l}NH\cdot CO\cdot NH_2\\ NH\cdot CHO\end{array} \longrightarrow$$
$$CO<\begin{array}{l}NH\cdot CO\cdot NH_2\\ NH_2\end{array} + H\cdot CO_2H\,.$$

The formation of biuret as well as of cyanuric acid when 5-bromoamino-5-hydroxyhydantoin is heated in aqueous solution is explained thus : the hydrogen bromide produced by the formation of cyanuric acid reacts with other molecules causing scission of hypobromous acid and reacts with this, liberating bromine, the

allantoxaidin thus set free then undergoing conversion into biuret; this view is confirmed by the observation that no biuret is formed when excess of hypobromite is present in the solution.

5-*Bromoamino-5-hydroxyhydantoin*, $C_3H_4O_3N_3Br$, forms poorly-developed crystals, m. p. about 143° (decomp.), and its *sodium* derivative, colourless needles. T. H. P.

3-Methyloxonic Acid and 3-Methylallantoxaidin. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1921, **54**, [*B*], 2448—2451).—The conversion of allantoin into oxonic (allantoxanic) acid and allantoxaidin finds a parallel in that of 3-methylallantoin (Behrend and Zieger, A., 1916, i, 164) into 3-methyloxonic acid and 3-methylallantoxaidin. The dimethylallantoxaidin obtained from diazomethane and allantoxaidin (A., 1920, i, 886) has m. p. 164°, and not 158° as previously given; since treatment of 3-methylallantoxaidin with diazomethane yields the same dimethyl derivative, one of the methyl groups of the latter must occupy the 3-position, but for the other methyl no choice is yet possible between the 1- and 6-positions.

3-*Methyloxonic* (3-*methylallantoxanic*) *acid*, $CO<\begin{matrix}NH{-}C{:}N{\cdot}CO_2H\\ NMe{\cdot}CO\end{matrix}$, forms short, indistinct crystals and loses carbon dioxide when heated, its apparent melting point being that of 3-methylallantoxaidin. It is obtained as the *potassium* salt when 3-methylallantoin is oxidised by permanganate in alkaline solution.

3-*Methylallantoxaidin*, $CO<\begin{matrix}NH{-}C{:}NH\\ NMe{\cdot}CO\end{matrix}$, crystallises in elongated prisms with oblique or roof-shaped ends, sintering at about 200°, m. p. 226°. Its conversion into α-methylbiuret has not yet been achieved.

An unsuccessful attempt has been made to transform 1-methylallantoin into 1-methyloxonic acid. T. H. P.

Allantoin and its Methyl Derivatives. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1921, **54**, [*B*], 2451—2476).—When subjected to prolonged boiling in aqueous solution, uric acid-4 : 5-glycol dimethyl ether yields allantoin, and similar behaviour is shown by the corresponding derivatives of various alkylated uric acids, although some of these either remain unchanged or give only the mono-ethers of the glycols. Thus, the glycol ethers of 1- and 7-methyluric acids yield 3-methylallantoin; that of 7-ethyluric acid, 3-ethylallantoin; those of 1 : 3- and 7 : 9-dimethyluric acids, 1 : 3-dimethylallantoin, and that of 1 : 7-dimethyluric acid, 3 : 8-dimethylallantoin. The glycol dimethyl ether of 3 : 7-dimethyluric acid gives the monomethyl ether, whilst those of 3 : 9-dimethyl-, 1 : 3 : 7-trimethyl-, and tetramethyl-uric acids remain unchanged. These glycols may undergo caffolide degradation, 3 : 7-dimethyluric acid-glycol, for instance, yielding 1-methyl-5-hydroxyhydantoylamide. The transformation of the uric acid–glycol ethers into allantoins may be accelerated by dissolving the ethers in alkali hydroxide solution, acidifying the solutions, and crystallising.

The various explanations which have been advanced of the mechanism of the formation of allantoin by the oxidation of uric acid in presence of alkali are discussed, the conclusion being drawn that the first and only intermediate product in this oxidation is hydroxyacetylenediureinecarboxylic acid (Behrend, A., 1904, i, 950). If the resulting strongly alkaline liquid is concentrated by evapor ation, even in the cold, potassium uroxanate crystallises out, this compound being formed by simple hydrolysis. If, however, the solution of the hydroxyacetylenediureinecarboxylic salt is acidified, the free acid loses its carboxyl group. The one ring, if possible that free from methyl groups, then appears to undergo immediate opening, displacement rearrangement giving the allantoin. The acidification is best effected by means of a weak acid, such as acetic acid, since evaporation of allantoin in presence of mineral acid results in its decomposition.

As regards the structure of allantoin, all the facts known previously, and likewise the results now obtained for the first time, are in complete agreement with the formula proposed by Grimaux (A., 1877, ii, 741), and Fenton and Wilks's reaction with monomethylfuryl (A., 1911, i, 269) also appears to support an open-chain formula. The available data are reconcilable with the hydroxyacetylenediureine formula only with difficulty, if at all. The optical inactivity always exhibited by allantoin may be due to extremely rapid racemisation.

3-*Ethylallantoin*, $\begin{matrix}CO\cdot NH\\ | \\ NEt\cdot CO\end{matrix}\!\!>CH\cdot NH\cdot CO\cdot NH_2$, prepared by boiling an aqueous solution of 4 : 5-dimethoxy-7-ethyl-4 : 5-dihydrouric acid (Biltz, Marwitzky, and Heyn, this vol., i, 606), crystallises in long, slender prisms with roof-like ends, m. p. 189—190° (slight frothing), and yields 3-ethylhydantoin when reduced by means of hydriodic acid.

1 : 3-*Dimethylallantoin*, $\begin{matrix}CO\cdot NMe\\ | \\ NMe\cdot CO\end{matrix}\!\!>CH\cdot NH\cdot CO\cdot NH_2$, crystallises in the triclinic system, in either rectangular prisms or flat, quadrilateral, double pyramids with truncated apices [S. Riedel: $a:b:c=2{\cdot}398:1:1{\cdot}306$; $\alpha=89°\ 7'$, $\beta=94°\ 5'$, $\gamma=98°\ 58'$], m. p. 214°, and yields 1 : 3-dimethylhydantoin on reduction by means of hydriodic acid.

5-*Hydroxy*-1-*methylhydantoylamide*, $C_5H_7O_4N_3$, obtained when an aqueous solution of 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid is boiled, crystallises in stout, mostly hexagonal plates [Beutell: apparently monoclinic], m. p. 203—204° (frothing and yellowing), and gives methylparabanic acid in good yield when oxidised.

1 : 8-*Dimethylallantoin*, $\begin{matrix}CO\cdot NMe\\ | \\ NH-CO\end{matrix}\!\!>CH\cdot NH\cdot CO\cdot NHMe$, prepared by heating an aqueous solution of 1 : 7-dimethyl*spiro*dihydantoin with basic lead acetate, forms stout, hexagonal crystals, m. p. 220—223° (evolution of gas and darkening), and is reduced to 1 methylhydantoin by hydriodic acid.

1 : 3 : 8-*Trimethylallantoin*, $C_7H_{12}O_3N_4$, prepared by the prolonged action of diazomethane on 1 : 8-dimethylallantoin, crystallises in narrow, flat prisms, sintering at 149°, m. p. 152°, and gives 1 : 3-dimethylhydantoin when treated with hydriodic acid.

Methylation of 1 : 6-dimethylallantoin by means of diazomethane yields 1 : 3 : 6-trimethylallantoin. T. H. P.

Stability of Uric Acid–Glycol Dimethyl Ether. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1921, **54**, [*B*], 2477—2479).—That certain samples of uric acid-4 : 5-glycol dimethyl ether (4 : 5-dimethoxy-4 : 5-dihydrouric acid) (cf. Biltz and Heyn, A., 1917, i, 286) yield, on prolonged boiling in aqueous solution, not allantoin, but uric acid-4 : 5-glycol monomethyl ether is found to be due to the fact that the dimethyl ether is not so stable as was previously thought and undergoes rapid transformation into 5-methoxy-ψ-uric acid if a small proportion of the hydrochloric acid formed during its preparation is left with the ether as impurity.
T. H. P.

The Coupling of Benzenoid Hydrocarbons with Diazo-compounds. KURT H. MEYER and HANS TOCHTERMANN (*Ber.*, 1921, **54**, [*B*], 2283—2285).—It has been shown previously (A., 1920, i, 97) that unsaturated aliphatic hydrocarbons couple with diazo-compounds to give crystalline azo-derivatives, but similar compounds have not been obtained previously with aromatic hydrocarbons, probably because the reaction occurs so slowly that the diazonium salt is decomposed before it has proceeded to a reasonable degree. It is now shown that the unusually reactive diazotised 2 : 4 : 6-trinitroaniline (prepared under the conditions described by Misslin, A., 1920, i, 887) couples readily with mesitylene to form 2 : 4 : 6-*trinitrobenzeneazomesitylene*,

$$C_6H_2(NO_2)_3\cdot N\colon N\cdot C_6H_2Me_3,$$

dark red, hexagonal platelets, m. p. 189° (decomp.), the constitution of which is deduced from its reduction to mesitylamine. Misslin's solution gives immediate intense colorations with toluene, *m*-xylene, α-methylnaphthalene, and anthracene which doubtless depend on the formation of azo-compounds, but the relative slowness of the action inhibits the isolation of the products; benzene, on the other hand, does not give a coloration. H. W.

Isonitriles. II. Compounds with Aldehydes or Ketones and Monobasic Organic Acids. M. PASSERINI (*Gazzetta*, 1921, **51**, ii, 181—188).—It has been shown (this vol., i, 743) that *p*-carbylaminoazobenzene reacts with acetone and acetic acid, giving rise to the acetyl derivative of hydroxy*iso*butyryl-*p*-aminoazobenzene. It is now found that a precisely similar reaction occurs with benzaldehyde, benzoic acid, and an *iso*nitrile. The reaction may, indeed, be regarded as general, the compound obtained undergoing progressive hydrolysis in accordance with the scheme: $NHR\cdot CO\cdot CR'R''\cdot O\cdot CO\cdot R'''$ (when an aldehyde is used, $R'=H$) $\longrightarrow$ $NHR\cdot CO\cdot CR'R''\cdot OH \longrightarrow CO_2H\cdot CR'R''\cdot OH$.

With ethyl acetoacetate, acetic acid, and *p*-carbylaminoazobenzene, the normal additive product is obtained, but when phenylcarbylamine is used, the hydrolysed product corresponding with acetoacetic acid results; the esterified product is doubtless formed first, but it is either liquid or too soluble to allow of isolation, and is hydrolysed by the excess of acetic acid present. The compounds obtained in these two cases are derivatives of citramalic acid and, when gradually hydrolysed by aqueous potassium hydroxide, give first derivatives of mesaconic or possibly citraconic acid, and finally mesaconic acid:

$$\mathrm{NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CMe(OAc){\cdot}CH_2{\cdot}CO_2Et} \rightarrow \mathrm{NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CMe{:}CH{\cdot}CO_2H} \rightarrow \begin{matrix}\mathrm{CO_2H{\cdot}C{\cdot}Me} \\ \| \\ \mathrm{H{\cdot}C{\cdot}CO_2H.}\end{matrix}$$

$$\mathrm{NHPh{\cdot}CO{\cdot}CMe(OAc){\cdot}CH_2{\cdot}CO_2H} \rightarrow \mathrm{NHPh{\cdot}CO{\cdot}CMe{:}CH{\cdot}CO_2H} \rightarrow$$

α-*Acetoxy*iso*butyranilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe_2{\cdot}OAc}$, prepared from phenylcarbylamine, acetone, and acetic acid, crystallises in slender colourless needles, m. p. 107—108°, and on hydrolysis yields α-hydroxy*iso*butyranilide (cf. Tigerstedt, A., 1893, i, 51).

Benzoyloxyphenylacetyl-p-*aminoazobenzene*,

$$\mathrm{NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CHPh{\cdot}OBz},$$

prepared from *p*-carbylaminoazobenzene, benzaldehyde, and benzoic acid, forms pale yellow crystals, m. p. 222°, and on hydrolysis yields

Mandelyl-p-*aminoazobenzene*, $\mathrm{NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CHPh{\cdot}OH}$, which crystallises in lustrous, copper-red scales, m. p. 186—188°.

Benzoyloxyphenylacetanilide, $\mathrm{NHPh{\cdot}CO{\cdot}CHPh{\cdot}OBz}$, obtained from phenylcarbylamine, benzaldehyde, and benzoic acid, crystallises in almost colourless, flat prisms, m. p. 177°, and is accompanied by a compound which separates in colourless needles, m. p. 161°, but was not further investigated. On hydrolysis, it yields mandelanilide (cf. Reissert and Kayser, A., 1891, i, 438).

Ethyl β-p-*aminoazobenzeneacetylcitramalate*,

$$\mathrm{NPh{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CMe(OAc){\cdot}CH_2{\cdot}CO_2Et},$$

obtained from ethyl acetoacetate, *p*-carbylaminoazobenzene, and acetic acid, crystallises in silky, yellow needles, m. p. 141°, and, when cautiously hydrolysed, yields either β-p-*aminoazobenzenemesaconic* or β-p-*aminoazobenzenecitraconic acid*, $C_{17}H_{15}O_3N_3$ (see above), as a yellow precipitate, m. p. 179°.

β-*Anilinoacetylcitramalic acid*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe(OAc){\cdot}CH_2{\cdot}CO_2H}$, forms crystals, m. p. 77—78°, and as first product of hydrolysis yields β-*anilinomesaconic* or β-*anilinocitraconic acid*, $C_{11}H_{11}O_3N$ (see above), crystallising in stout, highly refractive prisms, m. p. 165°. Two compounds different from each other and from that now obtained have been described as anilinomesaconic acid (cf. Michael and Palmer, A., 1886, 698; Anschütz and Reuter, A., 1890, 368).

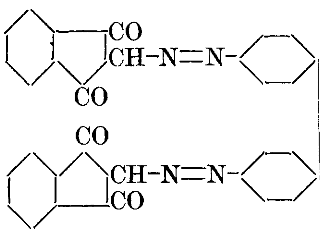
T. H. P.

Azo-compounds from Diketohydrindene. A. K. DAS and B. N. GHOSH (*J. Amer. Chem. Soc.*, 1921, **43**, 1739—1741).—Azo-compounds are formed by coupling diazonium compounds with 1 : 3-diketohydrindene in alkaline solution. The products

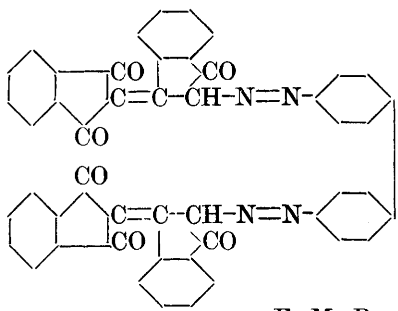
form insoluble sodium salts, but when applied to vegetable fibres in the usual manner for the production of insoluble azo-colours on the fibre fast shades are produced.

p-*Nitrobenzeneazo*-1 : 3-*diketohydrindene*, yellow crystals from pyridine, does not melt below 280°, and dissolves in sulphuric acid with a red colour and in potassium hydroxide with a magenta colour. p-*Tolueneazo*-1 : 3-*diketohydrindene*, yellow, silky flakes from acetic acid, m. p. 211°, dissolves in sulphuric acid with a chocolate colour. β-*Naphthaleneazo*-1 : 3-*diketohydrindene*, m. p. 205°, from acetic acid.

1 : 3-Diketohydrindene is readily converted into anhydro-bis-diketohydrindene. Thus, when tetrazotised benzidine is coupled with an alkaline solution of two molecular proportions of 1 : 3-diketohydrindene below 5°, *diphenylenebisazo*-1 : 3-*diketohydrindene* (I) is formed, whereas when the coupling is effected at 26°, *diphenylene-bisazo-anhydro-bisdiketohydrindene* (II) is formed.



(I.)



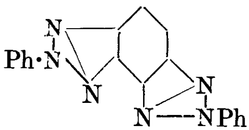
(II.)

F. M. R.

***pseudo*Azimides. I and II.** MAXIMILIAN P. SCHMIDT and ALFRED HAGENBÖCKER (*Ber.*, 1921, **54**, [*B*], 2191—2200, 2201—2209).—I. *o*-Aminoazo-compounds are readily oxidised to *pseudo*-azimides, but this behaviour is not shown by those substances which contain a further amino-group in the molecule. It is now shown that in these cases oxidation can be effected smoothly by ammoniacal cupric oxide solution, but it is noteworthy that four molecules of the oxidising agent are required for one molecule of dye instead of the two molecules calculated on the assumption of reduction to the cuprous stage.

5-Amino-2-phenyl-1 : 2 : 3-benztriazole, m. p. 182·5°, is obtained by boiling a suspension of benzeneazo-*m*-phenylenediamine in alcohol (50%) with an aqueous solution of copper sulphate which has been treated with excess of ammonia. Similarly, benzeneazo-*m*-tolylenediamine is transformed into 5-*amino*-2-*phenyl*-6-*methyl*-1 : 2 : 3-*benztriazole*, $NH_2\cdot C_6H_2Me<\overset{N}{\underset{N}{|}}>NPh$, m. p. 215°, and *p*-sulphobenzeneazo-*m*-phenylenediamine yields the *sodium* salt of 5-amino-2-sulphophenyl-1 : 2 : 3-benztriazole, needles which give an intense, yellowish-green, fluorescent solution (the corresponding *acid* is described). *p*-Nitrobenzeneazo-*m*-phenylenediamine, long,

red needles, m. p. 230°, is converted by copper sulphate in boiling aqueous pyridine solution into 5-*amino*-2-p-*nitrophenyl*-1 : 2 : 3-*benztriazole*, $NH_2\cdot C_6H_3<\substack{N\\|\\N}>N\cdot C_6H_4\cdot NO_2$, long, reddish-brown needles, m. p. 331°, which is reduced by zinc dust and glacial acetic acid to 5-*amino*-2-p-*aminophenyl*-1 : 2 : 3-*benztriazole*, m. p. 194°, which can be diazotised in the usual manner and couples normally with diazonium compounds (the *hydrochloride*, *sulphate*, and *acetyl* derivatives are described). 5-Amino-2-phenyl-1 : 2 : 3-benztriazole couples with benzenediazonium chloride to yield 4-*benzeneazo*-5-*amino*-2-*phenyl*-1 : 2 : 3-*benztriazole*, needles, m. p. 112° (the *hydrochloride* is described); the position of the azo-group is deduced from the similarity of the parent substance to β-naphthylamine. The dye is oxidised by lead peroxide in boiling xylene solution to 2 : 5-*diphenyl*-1 : 2 : 3 : 4 : 5 : 6-*benzditriazole* (annexed formula), four-sided, silvery plates or aggregates of needles, m. p. 221°.



5-Amino-2-sulphophenyl-1 : 3-benztriazole couples with diazotised sulphanilic acid, giving the *sodium* salt of 4-p-*sulphobenzeneazo*-5-*amino*-2-p-*sulphophenyl*-1 : 2 : 3-*benztriazole*, $C_{18}H_{12}O_6N_6S_2Na_2$, which is oxidised by ammoniacal copper solution to the *sodium* salt of 2 : 5-*di*-p-*sulphophenyl*-1 : 2 : 3 : 4 : 5 : 6-*benzditriazole*, $C_{18}H_{10}O_6N_6S_2Na_2$. 2-*Phenyl*-1 : 2 : 3-*benztriazole*-5-*azo*-β-*naphthylamine* (from diazotised 5-amino-2-phenyl-1 : 2 : 3-benztriazole and β-naphthylamine), small needles, m. p. 258°, is oxidised by lead peroxide in boiling xylene solution 5(2′ : 1′ : 3′-*naphthtriazolyl*)-2-*phenyl*-1 : 2 : 3-*benztriazole*, $C_{10}H_6<\substack{N\\|\\N}>N\cdot C_6H_3<\substack{N\\|\\N}>NPh$, silvery scales, m. p. 235°. Similarly, 4-β-*naphthaleneazo*-5-*amino*-2-*phenyl*-1 : 2 : 3-*benztriazole*, tile-red needles, m. p. 155—158°, gives 2-*phenyl*-5-β-*naphthyl*-1 : 2 : 3 : 4 : 5 : 6-*benzditriazole*,

$$C_{10}H_7\cdot N<\substack{N\\|\\N}>C_6H_2<\substack{N\\|\\N}>NPh,$$

m. p. 220°. Tetrazotised benzidine and β-naphthylamine give the *compound*, $C_{32}H_{24}N_6$, needles of metallic lustre, m. p. 315° (the corresponding *sulphate* is described), which is converted by copper powder or, but less advantageously, by lead peroxide in boiling nitrobenzene solution into the *di*-ψ-*azimide*,

$$C_{10}H_6<\substack{N\\|\\N}>N\cdot C_6H_4\cdot C_6H_4\cdot N<\substack{N\\|\\N}>C_{10}H_6,$$

colourless leaflets, m. p. 317°. The *substance*, $C_{24}H_{17}N_9$, tile-red crystals, m. p. 245° (decomp.), obtained by coupling 2-phenyl-1 : 2 : 3-benztriazole-5-diazonium sulphate with 5-amino-2-phenyl-1 : 2 : 3-benztriazole, is oxidised to 2-phenyl-5-(2′-phenyl-1′ : 2′ : 3′-benztriazolyl-5′)-1 : 2 : 3 : 4 : 5 : 6-benzditriazole,

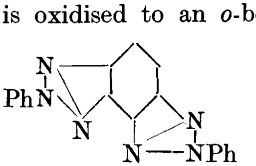
$$PhN<\substack{N\\|\\N}>C_6H_2<\substack{N\\|\\N}>N\cdot C_6H_3<\substack{N\\|\\N}>NPh,$$

small leaflets, m. p. 231°.

II. *m*-Phenylenediamine readily couples with two molecules

of a diazonium compound with the formation of bisazo-dyes, but the point of attachment of the second diazonium residue has not been placed beyond doubt. Since the dyes do not suffer fission in the normal manner, the authors have endeavoured to elucidate the problem by converting them into ditriazoles. It is found that the "double coupling" of *m*-phenylenediamine takes place in a more complex manner than was previously supposed and that, under the customary conditions of the reaction, the second diazonium residue becomes attached in about an equal degree to the 2- and 6-positions of *m*-phenylenediamine, thus yielding two bisazo-dyes which are oxidisable to two ditriazoles.

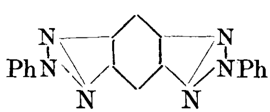
It has been shown already that the azo-dye derived from benzenediazonium chloride and 5-amino-2-phenyl-1 : 2 : 3-benztriazole is oxidised to an *o*-benzditriazole which must have the annexed formula if the diazonium residue enters the molecule in position 4. This was considered to be the case by reason of the similarity of the amine to β-naphthylamine, but a more definite proof is obtained in the following manner. 5-Amino-2-phenyl-6-methyl-1:2:3-benztriazole reacts with benzenediazonium chloride to form 4-*benzeneazo-5-amino-2-phenyl-6-methyl-1 : 2 : 3-benztriazole,* yellowish-red crystals, m. p. 165°, in which the new group must have entered in position 4, since coupling in the meta-position has never been observed. If, however, the position 4′ is occupied by a methyl group as in 5-*amino-2-phenyl-4-methyl-1 : 2 : 3-benztriazole,* coarse prisms, m. p. 126° (obtained by the oxidation of 3-*benzeneazo-2 : 6-tolylenediamine,* needles, m. p. 124°), the action of a diazotised solution of *p*-nitroaniline does not lead to the production of an azo-dye but to the diazoamino-compound



$$PhN<\overset{N}{\underset{N}{|}}>C_6H_2Me\cdot N:N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which is converted by concentrated sulphuric acid into *p*-nitroaniline and 2-phenyl-4-methyl-1 : 2 : 3-benztriazole-5-diazonium sulphate.

The action of benzenediazonium chloride on benzeneazo-*m*-phenylenediamine leads to the formation of a mixture of 2 : 4-dibenzeneazo-*m*-phenylenediamine, m. p. 250° (discovered by Griess), and 2 : 6-*dibenzeneazo*-m-*phenylenediamine,* red needles, m. p. 159°; the constitution of the former is deduced from the observation that it is converted by copper sulphate in aqueous pyridine solution into a ditriazole which is not identical with the ortho-compound described above and which therefore must be 2 : 6-*diphenyl-1 : 2 : 3 : 5 : 6 : 7-benzditriazole* (annexed formula), m. p. 334°, whereas the isomeride, m. p. 159°, is transformed into 2 : 5-diphenyl-1 : 2 : 3 : 4 : 5 : 6-benzditriazole, m. p. 221°.



3 : 5-*Dibenzeneazo-2 : 4-tolylenediamine,* long, red needles, m. p. 135° (from benzeneazotolylenediamine and benzenediazonium chloride), is oxidised by copper sulphate in aqueous pyridine

solution to 2 : 5-*diphenyl*-7-*methyl*-1 : 2 : 3 : 4 : 5 : 6-*benzditriazole*, m. p. 192°, which is also obtained by the action of lead peroxide on 4-benzeneazo-5-amino-2-phenyl-6-methyl-1 : 3-benztriazole in boiling xylene. H. W.

Azides of Thiocarbamic Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, **51**, ii, 195—201).—In conjunction with Noto, the author has shown (A., 1913, i, 774) that the action of azoimide on phenylthiocarbimide at 40° yields the compound described by Freund and Hempel (A., 1895, i, 193) as 3-thio-4-phenyltetrazoline. This compound does not, however, correspond in chemical behaviour with such a structure and the author regards it as the azide of phenylthiocarbamic acid, $NHPh{\cdot}CS{\cdot}N_3$, analogous to the azides of carbamic acid. The mechanism of the addition of azoimide to thiocarbimides would then be similar to that of its addition to carbimides and to ketens: $R{\cdot}N{:}C{:}S+N_3H=R{\cdot}NH{\cdot}CS{\cdot}N_3$; $R{\cdot}N{:}C{:}O+N_3H=R{\cdot}NH{\cdot}CO{\cdot}N_3$ and $R_2{:}C{:}C{:}O+N_3H=R_2{:}CH{\cdot}CO{\cdot}N_3$. Further, the reaction between nitrous acid and a thiosemicarbazide, $NHR{\cdot}CS{\cdot}NH{\cdot}NH_2+HNO_2 \longrightarrow NHR{\cdot}CS{\cdot}N_3$, becomes analogous to Curtius's reaction between nitrous acid and a semicarbazide. Again, just as Curtius and Burkhardt (A., 1899, i, 137) observed with azides of the carbamic acids, these azides of thiocarbamic acids are found to lose their triazo-group as azoimide when treated with ammonia, aniline, or phenylhydrazine, derivatives of thiocarbamide being thus formed. On the other hand, the azides of thiocarbamic acids are distinguished from those of carbamic acids by the great mobility of their triazo-groups. Thus, alkalis convert them into isomeric tetrazole derivatives, $NHR{\cdot}CS{\cdot}N_3 \longrightarrow \begin{matrix}NR\text{—}N\\ |\\ C(SH){:}N\end{matrix}\!\!>\!N$, whilst treatment with hydrochloric acid results in the loss of two nitrogen atoms from the molecule and heating in an indifferent solvent in the elimination of an atom of sulphur, $NHR{\cdot}CS{\cdot}N_3 \longrightarrow NHR{\cdot}C{<}\begin{matrix}S\\ |\\ N\end{matrix} \longrightarrow NHR{\cdot}CN$.

The azide of phenylthiocarbamic acid yields phenylthiocarbamide when treated with concentrated aqueous ammonia, and diphenylthiocarbamide when treated with alcoholic aniline.

The *azide* of o-*tolylthiocarbamic acid*, $C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}N_3$, prepared from *o*-tolylthiocarbimide and azoimide, crystallises in large, thin plates, m. p. 120° (decomp.), and is highly sensitive to the action of light, which gradually turns it red. When heated with alcoholic ammonia under pressure, it gives o-*tolylthiocarbamide*, $C_7H_7{\cdot}NH{\cdot}CS{\cdot}NH_2$, which forms crystals, m. p. 154—155°.

1-o-*Tolyltetrazole*-5-*thiol*, $C_6H_4Me{\cdot}N{<}\begin{matrix}C(SH){:}N\\ N{=\!=}N\end{matrix}$, obtained by isomeric change of the preceding compound under the action of alkali, forms crystals, m. p. 129°. When oxidised by means of ferric chloride in alcoholic solution, it appears to yield the disulphide, $C_7H_7{\cdot}CN_4{\cdot}S{\cdot}S{\cdot}CN_4{\cdot}C_7H_7$, which was not isolated owing to lack of material. By alkaline permanganate solution it is, however, converted in the cold into 1-o-*tolyltetrazole*-5-*sulphonic acid*,

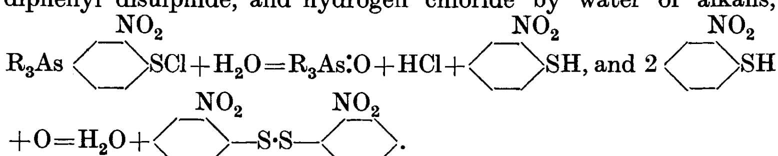
$C_7H_7{\cdot}CN_4{\cdot}SO_3H$, which was isolated as the *potassium* salt, and in the hot into *5-hydroxytetrazole-1-benzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CN_4{\cdot}OH$, which begins to decompose slowly when heated above 200° and in appearance closely resembles its para-isomeride (*loc. cit.*).

T. H. P.

Action of Sulphur Monochloride on Tertiary Aromatic Arsines: Constitution of Sulphur Monochloride. FRITZ ZUCKERKANDL and MARTHA SINAI (*Ber.*, 1921, **54**, [*B*], 2479—2489).—The action of sulphur monochloride on tertiary aromatic arsines, which, if similar to that on triphenylbismuthine (Challenger, T., 1916, **109**, 250), might be used for the preparation of arsine dichlorides not obtainable by the action of chlorine on tertiary arsines, actually proceeds quite differently. In an indifferent solvent, the reaction yields an additive compound, AsR_3,S_2Cl_2, which is instantly decomposed by water or alkali, $AsR_3,S_2Cl_2+H_2O=2HCl+S_2+R_3As{:}O$, and is converted into the corresponding sulphide, $R_3As{:}S$, by either hydrogen sulphide or ammonium pentasulphide.

This new method for obtaining tertiary aromatic arsine oxides and sulphides has been applied to the preparation of triphenylarsine hydroxide and sulphide, tri-α-naphthylarsine hydroxide (Michaelis, A., 1902, i, 517, 524), tri-α-naphthylarsine sulphide, *pp'p''*-hexamethyltriaminotriphenylarsine oxide and sulphide. The additive compounds with sulphur chloride vary greatly in stability, but they need not be isolated, and the yields of arsine oxide and sulphide are very good. That such compounds are actually additive and not merely molecular in character is shown by the fact that they always decompose into derivatives of quinquevalent arsenic.

Of the three possible structures for such additive compounds, namely, $AsR_3{:}S{:}SCl_2$, $AsR_3Cl{\cdot}S{\cdot}S{\cdot}Cl$, and $AsR_3(SCl)_2$, the second is regarded as the most probably accurate (cf. Lecher, A., 1920, i, 433; von Konek, A., 1920, i, 880), this involving the assumption that sulphur chloride has the simple disulphide formula, $Cl{\cdot}S{\cdot}S{\cdot}Cl$. That such assumption is justified is shown by the interaction of *o*-nitrophenylsulphur chloride, $NO_2{\cdot}C_6H_4{\cdot}S{\cdot}Cl$ (Zincke and Farr, A., 1912, i, 763) on *pp'p''*-hexamethyltriaminotriphenylarsine, which also yields an additive compound, decomposed immediately into hexamethyltriaminotriphenylarsine oxide, *oo'*-dinitrodiphenyl disulphide, and hydrogen chloride by water or alkalis,



To the additive compound is ascribed the formula

$$(NMe_2{\cdot}C_6H_4)_3AsCl{\cdot}S{\cdot}C_6H_4{\cdot}NO_2,$$

since if the chlorine were united to sulphur as in

$$(NMe_2{\cdot}C_6H_4)_3As{:}SCl{\cdot}C_6H_4{\cdot}NO_2,$$

the action of water should yield *o* : *o'*-dinitrodiphenylsulphur oxide,

$O(S\cdot C_6H_4\cdot NO_2)_2$, or even the corresponding disulphoxide or sulphinic acid, $NO_2\cdot C_6H_4\cdot SO_2H$; such sulphur oxides are formed, for instance, by the action of water or alkali on *o*-nitrophenylsulphur chloride (Zincke and Farr, *loc. cit.*).

It has not been found possible to prepare the intermediate product, $PPh_3Cl\cdot S\cdot S\cdot Cl$, from triphenylphosphine (Pfeiffer, Hiller, and Pietsch, A., 1905, i, 164). This result conforms exactly with Steinkopf and Buchheim's observation that tertiary arsines combine with cyanogen bromide to form relatively stable arsinebromocyanides, whereas the corresponding compound formed by triphenylphosphine is unstable and could not be isolated (this vol., i, 469).

The *additive* compound, $AsPh_3Cl\cdot S\cdot S\cdot Cl$, formed by triphenylarsine and sulphur chloride, forms yellowish-white crystals, m. p. 200°, a minimal addition of free sulphur lowering the melting point to below 110°; when boiled with ammonia solution, triphenylarsine hydroxide is formed.

The *additive* compound, $(NMe_2\cdot C_6H_4)_3AsCl\cdot S\cdot S\cdot Cl$, obtained from *pp′p″*-hexamethyltriaminotriphenylarsine and sulphur chloride, forms crystals, m. p. 137—141°.

pp′p″-*Hexamethyltriaminotriphenylarsine dihydroxide*,

$$(NMe_2\cdot C_6H_4)_3As(OH)_2,$$

crystallises in cubes, m. p. 257°. The corresponding *oxide*, $(NMe_2\cdot C_6H_4)_3As{:}O$, forms white crystals, m. p. 277°, and the *sulphide*, $C_{24}H_{30}N_3SAs$, glistening leaflets, m. p. 269—270°.

The *additive* compound, $(NMe_2\cdot C_6H_4)_3AsCl\cdot S\cdot C_6H_4\cdot NO_2$, formed by hexamethyltriaminotriphenylarsine and *o*-nitrophenylsulphur chloride, forms crystals, m. p. 201° (decomp.).

Tri-α-naphthylarsine, obtained by Michaelis (*loc. cit.*) in 20% yield, may be obtained in 46% yield from α-bromonaphthalene, magnesium, and arsenic trichloride. The *additive* compound with sulphur chloride, $C_{30}H_{21}Cl_2S_2As$, forms crystals, m. p. 175° (decomp.). Tri-α-naphthylarsine dihydroxide and the *sulphide*, $As(C_{10}H_7)_3{:}S$, which forms white leaflets, m. p. 285°, were prepared. T. H. P.

Action of Mercuric Acetate on *p*-Toluidine. II. L. VECCHIOTTI (*Gazzetta*, 1921, **51**, ii, 208—210).—In order to ascertain the position of the mercury group in the molecule of *p*-toluidinemercuriacetate (A., 1919, i, 103) in relation to the amino-group, the author acetylates the latter and treats the acetyl derivative with bromine in acetic acid solution, the resulting product being *m*-bromo-*p*-acetotoluidide, m. p. 118° (Wroblewsky, *Annalen*, 1861, **118**, 152). Thus, when the para-position is occupied by either mercury or methyl, a second mercury atom entering the nucleus always goes to the ortho-position with reference to the amino-group.

The *acetyl* derivative of *p*-toluidinemercuriacetate,

$$NHAc\cdot C_6H_3Me\cdot Hg\cdot OAc,$$

forms colourless, highly refractive, prismatic crystals, m. p. 175°.
T. H. P.

Complex Salts of Mercury with Phenols. V. PAOLINI (*Gazzetta*, 1921, **51**, ii, 188—194).—According to Merck (*Arch.*

Pharm., 1893, **231**, 124), the compound obtained by the interaction of thymol and mercuric acetate consists of two molecules of mercuric acetate, in one of which one of the acetyl groups is replaced by a thymyl residue, $Hg(OAc)_2+OAc{\cdot}Hg{\cdot}O{\cdot}C_{10}H_{13}$. The existence of such compounds is, however, doubtful, and their constitution cannot be determined by their elementary composition alone (Schmidt, *Pharmazeutische Chemie*, 1911, ii, 1099). The author has prepared a mercuric acetate–thymol compound which contains non-ionisable mercury united directly to the carbon of the nucleus, the compound being readily and completely soluble in dilute sodium hydroxide and precipitated unchanged on addition of an acid. Treatment of this compound with aqueous sodium chloride yields the corresponding mercuric chloride compound, from which the two HgCl residues are displaced by two iodine atoms when the compound is treated with a solution of iodine in aqueous potassium iodide. The formation of the original compound and these transformations are represented by the equations: $OH{\cdot}C_6H_3MePr + 2Hg(OAc)_2 = 2AcOH + OH{\cdot}C_6HMePr(Hg{\cdot}OAc)_2$; $OH{\cdot}C_6HMePr(Hg{\cdot}OAc)_2+2NaCl=2CH_3{\cdot}CO_2Na+OH{\cdot}C_6HMePr(HgCl)_2$, and $OH{\cdot}C_6HMePr(HgCl)_2+2I_2=2HgClI+OH{\cdot}C_6HI_2MePr$. Merck's compound also undergoes these changes and differs from that obtained by the author in that it is contaminated with free thymol.

Phenol yields a similar compound, from which a di-iodophenol may be obtained. On the other hand, β-naphthol and vanillin, although they react promptly with a cold saturated solution of mercuric acetate in acetic acid, give only mono-substituted products, from which, by way of the chloro-compounds, an iodonaphthol and an iodovanillin are obtainable.

Diacetatomercurithymol, $OH{\cdot}C_{10}H_{11}(Hg{\cdot}OAc)_2$, prepared from thymol and a saturated solution of mercuric acetate in acetic acid, forms lustrous crystals and its *sodium* derivative large plates.

Dichloromercurithymol, $OH{\cdot}C_{10}H_{11}(HgCl)_2$, yields thymol when reduced by means of zinc and potassium hydroxide; the *di-iodothymol*, $C_{10}H_{11}I_2{\cdot}OH$, is an almost colourless oil, b. p. 215°/16 mm. (partial decomp.).

Diacetatomercuriphenol, $OH{\cdot}C_6H_3(Hg{\cdot}OAc)_2$, forms crystals, and *dimercurichlorophenol*, $OH{\cdot}C_6H_3(HgCl)_2$, yields the di-iodophenol described by Hlasiwetz (*Ber.*, 1869, **2**, 524) when treated with a solution of iodine in aqueous potassium iodide.

Acetatomercuri-β-naphthol, $OH{\cdot}C_{10}H_6{\cdot}Hg{\cdot}OAc$, crystallises in lustrous needles, and, without dissolving or changing in appearance, is converted by aqueous sodium chloride into *chloromercuri-β-naphthol*, $OH{\cdot}C_{10}H_6{\cdot}HgCl$, which may then be transformed into 1-iodo-β-naphthol (cf. Meldola, T., 1885, **47**, 525).

Acetatomercurivanillin, $C_8H_7O_3{\cdot}Hg{\cdot}OAc$, separates in crystals, and *chloromercurivanillin*, $C_8H_7O_3{\cdot}HgCl$, yields the iodovanillin obtained by Carles (*Ber.*, 1874, **7**, 616) from vanillin and alcoholic iodine solution. T. H. P.

Physiological Chemistry.

The Regulation of the Reaction of the Blood. C. L. EVANS (*J. Physiol.*, 1921, **55**, 159—192; from *Physiol. Abstr.*, 1921, **6**, 424).—The buffering of separated plasma (primary buffering) is contrasted with that induced in the true plasma of whole blood through the agency of the red corpuscles (secondary). The reaction of plasma, although dependent on the ratio of free to fixed carbon dioxide, is not wholly determined by this, but also by the other salts present, which lower the reaction by P_H 0·3. The effect of plasma proteins as buffers is negligible in practice. A slight modification of the Hasselbalch formula, with the use of values for $P{\cdot}K_1$ derived from observations made on plasma, allows of the calculation of the reaction of a plasma from the usual data. The carbon dioxide reaction curves for plasmata of varying bicarbonate content are parallel, whilst the P_H at a given carbon dioxide pressure varies directly as the logarithm of the bicarbonate content as for bicarbonate solutions; these relations are much less accurately maintained when whole blood is dealt with, first, because of differences in the extent and range of secondary buffering; secondly, because of capricious post-mortem changes in the corpuscles. Blood of high hæmoglobin or of low bicarbonate content has a flatter carbon dioxide reaction curve than that in which either or both of these proportions is reversed. When a blood shows a reduction of carbon dioxide capacity on keeping, this change affects the corpuscles more than the true plasma, which tends to maintain a constant bicarbonate content at a given carbon dioxide pressure; this is yet another instance of the operation of secondary buffering in all circumstances which otherwise would tend to lower the P_H of the blood (plasma). Plasma, blood, and bicarbonate solutions alike are more alkaline at higher than at lower temperatures. E. S.

Regulation of the Alkalinity of the Blood. J. B. S. HALDANE (*J. Physiol.*, 1921, **55**, 265—275; from *Physiol. Abstr.*, 1921, **6**, 424—425).—Ingestion of 5 to 55 grams of ammonium chloride in man causes a fall in the alveolar carbon dioxide and in the blood carbon dioxide capacity, and a rise in the acid, ammonia, and phosphate of the urine. The depression of the alveolar carbon dioxide is roughly proportional to the rate of excretion of acid plus ammonia. The ratio of acid to ammonia depends on the amount of phosphate available for excretion, and this amount falls as the acidosis progresses. The various effects are probably due to conversion of part of the ammonium chloride into urea, thus freeing the hydrochloric acid. E. S.

Physico-Chemical State of Sugar in the Blood. K. ONOHARA (*Brit. J. Expt. Path.*, 1921, **2**, 194—196; from *Physiol. Abstr.*, 1921, **6**, 440—441).—As shown by Kozawa, dextrose causes swelling of

human red corpuscles. Practically the same hematocrite results, however, were obtained with human red corpuscles treated with the serum of a diabetic patient, normal serum with the addition of isotonic dextrose solution, or isotonic dextrose–saline solution. It may therefore be assumed that sugar in the circulating blood is present in the same physico-chemical character as in the solution of free dextrose, that is, it is present as free sugar. E. S.

The Dextrose Content of Arterial and Venous Blood from Muscle. R. EGE and V. HENRIQUES (*Compt. rend. Soc. Biol.*, 1921, **85**, 610—611; from *Physiol. Abstr.*, 1921, **6**, 441).—The experiments were conducted on the hind-limb of the goat and dog after preparation of the animals by fasting and administration of phloridzin to remove all stores of carbohydrate. Under these conditions, the arterial blood-sugar was 0·004%, while the venous blood-sugar was one-fifth of this, namely, 0·0008%. E. S.

Coagulation of the Blood. II. The Clotting Complex. H. W. C. VINES (*J. Physiol.*, 1921, **55**, 287—295; from *Physiol. Abstr.*, 1921, **6**, 424).—The clotting complex (cf. this vol., i, 525) is a combination of a lipoid, calcium, and a protein. The calcium–lipoid combination is essential, and does not yield calcium ions; the function of the protein, which seems to render the lipoid compound more sensitive and may act by keeping it in a state of fine suspension, is apparently secondary. The compound has properties resembling those of the thrombokinase of Morawitz rather than of the prothrombin of Howell. The anti-coagulants (oxalates, citrates, fluorides, hirudin, and cobra venom) act as antikinase; hirudin acts also as an antithrombin. E. S.

The Chloride Content of the Serum of Sucklings. K. SCHEER (*Jahrb. Kinderheilk.*, 1921, **94/44**, 295—314; from *Physiol. Abstr.*, 1921, **6**, 426).—The chloride content of the serum of sucklings is fairly constant, and about 0·50 to 0·59%. At the beginning of digestion, the chloride decreases quickly, and regains its former level afterwards. This connexion between the serum chloride and the secretion of gastric juice is quite independent of the kind of food. Infusion of isotonic dextrose solution effects a diminution of the serum chlorides of some hours' duration. E. S.

A Method for Investigating the Hæmolytic Activity of Chemical Substances. ERIC PONDER (*Proc. Roy. Soc.*, 1921, [*B*], **92**, 285—295).—A new technique is described. Estimations of the hæmolytic activity of a number of substances indicate that, for a constant quantity of hæmolytic substance, the relation between temperature and time of hæmolysis is expressed by a hyperbola. E. S.

The Calcium Content of Egg-white. HANS KREIS and JOSEF STUDINGER (*Schweiz. Apoth. Zeit.*, 1921, **59**, 193—196).—White of fresh hens' eggs yields 0·75—0·80% of ash containing 0·59—4·25% of calcium oxide; the lime content of the ash of egg-yolk is 11·54—12·32%. When preserved in calcium hydroxide solution,

lime is not absorbed, so that estimations of calcium in the ash of the albumin give no indication of such preservation (cf. Rözenyi, *Chem. Zeit.*, 1904, **28**, 620). CHEMICAL ABSTRACTS.

Composition of the Egg of the Brown Frog (*Rana fusca*) at the Time of Laying. E. F. TERROINE and H. BARTHÉLÉMY (*Compt. rend.*, 1921, **173**, 611—613).—The composition of the ovarian eggs of the brown frog at the time of laying is remarkably constant and is independent of the age, weight, etc., of the individual females. The organic matter of the egg is almost entirely composed of nitrogenous substances, fats, and lipoids. There is a remarkable similarity in composition between the eggs of the frog and those of the trout and silk-worms. W. G.

Is Glycogen the Source of the Acids developed in Autolysis? W. MORSE (*Proc. Soc. Expt. Biol. Med.*, 1921, **18**, 246—247; from *Physiol Abstr.*, 1921, **6**, 406).—Ox liver was used for the experiments on autolysis. The results indicate that glycogen may be one of the precursors of substances concerned with the development of acidity. E. S.

Internal Secretion of the Spleen. N. B. EDDY (*Endocrin.*, 1921, **5**, 461—475; from *Physiol. Abstr.*, 1921, **6**, 448).—It is claimed that the spleen produces an internal secretion which regulates the number of red corpuscles in the blood-stream. This is supported by the changes in the erythrocytes after splenectomy; the modification of the blood-picture in hyperplasia of the spleen, ameliorated in some cases by splenectomy, and the specific effects on the red corpuscles of injection of splenic extract. It is suggested that the chief function of the spleen is the removal from the circulation of the disintegrated erythrocytes; that the splenic cells elaborate this material, producing thereby an internal secretion, which was a component of the erythrocyte, either stroma or pigment portion; that this internal secretion reduces the resistance of all the red blood-corpuscles, the effect amounting to actual destruction of the older cells, and, finally, that this internal secretion, possibly after modification by the liver, stimulates the erythrogenic function of the bone-marrow, and is used up in the manufacture of new corpuscles. E. S.

Creatinine and Creatine in Muscle Extracts. I. A Comparison of the Picric Acid and the Tungstic Acid Methods of Deproteinisation. II. The Influence of the Reaction of the Medium on the Creatinine–Creatine Balance in Incubated Extracts of Muscle Tissue of the Albino Rat. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1921, **48**, 127—131 and 133—141).—The author describes procedures whereby concordant results in the estimation of creatinine in muscle extracts may be obtained by the use of either picric acid or tungstic acid as protein precipitants. Using the picric acid method, he finds that, if extracts of the muscle tissue of the rat are incubated at body temperature, the creatinine increases at the expense of the creatine. This change is influenced by the reaction of the medium, the optimum effect

being obtained when this is buffered to neutrality by a phosphate mixture. The presence of an enzyme capable of bringing about this change is suggested but not proved (cf. Hahn and Barkan, this vol., i, 515). C. R. H.

Action of various Lactones on Worm Muscles. LUDWIG LAUTENSCHLÄGER (*Ber. deut. Pharm. Ges.*, 1921, **31**, 279—291).—Further experimental support is adduced of Trendelenburg's theory (*Arch. Expt. Path. Pharm.*, 1915, **79**, 190) that the anthelmintic action of santonin and similarly constituted compounds is to be ascribed to the lactone structure, and comparative experiments have shown further that the lactone group must be associated with a carbon ring system, open-chain lactones having no anthelmintic action. The naphthalene nucleus in santonin can be replaced by a simpler cyclic system, so, for example, phthalide and meconin (dimethoxyphthalide) are as powerful in their action as santonin, and the replacement of one of the methylene hydrogen atoms by a simple alkyl group still further increases their activity. On the other hand, substitution by an aromatic group produces a decided weakening in the anthelmintic action. G. F. M.

Distribution of Sodium Salts in Plant and Animal Cells. S. FUNCOKA (*Kyoto Igaku Zasshi*, 1918, **15**, 85—120).—Sodium may be detected by precipitation as a double sulphate with cerium, or as a triple magnesium and uranyl acetate; a negative result does not exclude the presence of sodium. By these and other reactions, sodium was found in the blood plasma of both vertebrates and invertebrates, but not in their erythrocytes. It was present in the lymph of muscles but not in their fibres. Sodium occurred in the ground substance of cartilage but not in the cells themselves. In other tissues, it was detected in the intercellular substance but not in the cells. In plants, sodium was found in the cell plasma, but not in the nucleus or the chlorophyll bodies.

CHEMICAL ABSTRACTS.

The Variation in the Zinc Content of the Rabbit's Body during Growth. GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1921, [iv], **29**, 915—917).—In the case of the rabbit, the percentage of zinc present in the whole body shows a maximum at the moment of birth, diminishing gradually during the time of suckling, and then rising rapidly after weaning. W. G.

The Distribution of Zinc in the Organism of the Fish. M. BODANSKY (*Compt. rend.*, 1921, **173**, 790—792; cf. this vol., i, 78).—In the red snapper fish, *Lutjanus aya*, the liver and the spleen are the most important centres of accumulation of zinc, and the skeletal portions as well as the branchial arcs, the skin and the fins, contain relatively more zinc than the other tissues such as the muscles. In the catfish, *Ailurichtys marinus*, the branchial arcs and the skeleton have the highest zinc content, followed by the liver, the fins, and the skin, whilst again the muscles contain but little zinc. W. G

Calcium in the Blood in Diseases of the Skin. W. C. THRO and MARIE EHN (*Proc. Soc. Expt. Biol. Med.*, 1920, **17**, 115—118, and *ibid.*, 1921, **18**, 189—191).—Gravimetric methods for the estimation of calcium in the blood were vitiated by the presence of calcium in filter-paper; Halverson and Bergeim's volumetric method was therefore subsequently employed. The blood plasma of normal persons contained from 7·8 to 9·8 mg. of calcium per 100 c.c. The average amount of calcium present was low in cases of furunculosis diabetes, hemophilia, and puerpura hæmorrhagia, normal in cases of hemiplagia, secondary anæmia, pneumonia, and familial paralysis, and high in cases of acne, healed pulmonary tuberculosis, and some cases of nephritis. CHEMICAL ABSTRACTS.

Chemotherapeutic Experiments with "Bayer 205," a New Trypanocidal Agent of Special Activity. L. HAENDEL and K. W. JOETTEN (*Berl. Klin. Woch.*, 1920, **57**, ii, 821—823).—0·5 Mg. of the agent causes the permanent disappearance of *Trypanosoma brucei* from mice, for which the lethal dose is 20 mg. Remarkable cures are also effected in the case of the dourine disease of horses. Some trypanosomes are not eliminated, for example, *T. lewisii*. Cf. the two following abstracts. G. B.

Experiments with a New Trypanocidal Agent ("Bayer 205") on Trypanosomes Pathogenic to Man and to Animals. MARTIN MAYER and HEINZ ZEISS (*Arch. Schiffs-u. Tropenhygiene*, 1920, **24**, 257—294; cf. preceding abstract).—The curative subcutaneous dose for mice is 0·06 mg., the lethal dose 10 mg. The substance is an unfailing therapeutic agent for mice, rats, guinea-pigs, and rabbits infected with *T. brucei* (Nagana), *T. equiperdum*, *T. equinum*, *T. gambiense* (human sleeping sickness), and *T. rhodesiense*. Smaller doses have a prolonged prophylactic effect. G. B.

Action of "Bayer 205" on *Trypanosoma equiperdum* in Experimentally Infected Mice. C. M. WENYON (*Brit. Med. J.*, 1921, ii, 746; cf. preceding abstract).—0·005 Gram per kilo given intravenously frees mice from *T. equiperdum* in the course of forty-eight hours. G. B.

Action of Bismuth on Syphilis and on Nagana trypanosomiasis. Treatment of Syphilis by Bismuth. R. SAZERAC and C. LEVADITI (*Compt. rend.*, 1921, **172**, 1391; **173**, 338).—Sodium bismuth tartrate, suspended in oil, has a very favourable effect on syphilis in rabbits and in man; it is much less effective on Nagana. G. B.

Treatment of Syphilis by Bismuth. LOUIS FOURNIER and L. GUÉNOT (*Compt. rend.*, 1921, **173**, 674—676).—Results obtained with human syphilis amply confirm the conclusions of the preceding abstract; bismuth is a most promising agent. G. B.

The Fate of Salicylic Acid and some of its Derivatives in the Organism. W. DEVRIENT (*Arch. expt. Path. Pharm.*, 1921, **90**, 242—255; from *Physiol. Abstr.*, 1921, **6**, 439).—Not more than 15% of the salicylic acid administered is excreted in the urine. Sauerland's method of estimating it is found to be exact. E. S.

The Antipyretic Action of some Derivatives of Dimethylphenetidine. HEINRICH RHODE (*Ber. deut. Pharm. Ges.*, 1921, **31**, 271—279).—In the dimethylphenetidine series, as in the phenetidine series, the acetyl derivative has a much stronger antipyretic action than the other acyl derivatives, but it is nevertheless considerably weaker than phenacetin in its fever-reducing properties. Although phenetidine is stronger in its action than phenacetin, yet dimethylphenetidine is weaker than phenacetin, but it is noteworthy that experiments on rabbits free from fever showed a greater reduction in temperature after administration of the former than after an equal dose of the latter. Aryldimethylphenetidines such as the acetylsalicoyl- or *p*-aminobenzoyl-derivatives are stronger in their action than formyl- or valeryl-dimethylphenetidine, but weaker than the acetyl derivative or dimethylphenetidine itself. Finally, although phenetidine is a stronger febrifuge than phenacetin, yet ethoxydimethylphenacetin is more powerful than diethoxydimethylphenetidine. No logical connexion can therefore be traced between the chemical constitution and the physiological action of these phenetidine derivatives.

G. F. M.

Chemistry of Vegetable Physiology and Agriculture.

Physiology of Methane Bacteria. E. MÜNZ (*Halle Diss.*, 1915, 61 pp.; from *Bied. Zentr.*, 1921, **50**, 390).—*Bacterium methanicum* (Söhngen's *Bacillus methanicus*) has minimum 18°, maximum 40°, optimum 34°. The most favourable conditions for its activity are high methane and low oxygen concentration, the optimum oxygen concentration being 2%; light is without influence on the absorption of methane. Under autotrophic conditions, it multiplies and produces organic matter. Although other hydrocarbons and carbon monoxide cannot be substituted for methane, alcohols, carbohydrates, and salts of organic acids giving rise to hydrocarbons may be utilised. Nitrogen is utilised both in inorganic forms (nitrates and ammonium salts) and in organic forms (peptone, leucine, asparagine). The organisms may also live heterotrophically.

G. W. R.

The Micro-organisms Producing Acetone. ALBERT BERTHELOT and (MLLE) E. OSSART (*Compt. rend.*, 1921, **173**, 792—794).—In addition to the anærobic organisms used by Fernbach

in the manufacture of acetone, there exist, widely distributed in nature, many other organisms, both ærobic and facultative anærobes, capable of producing acetone, although to a smaller extent. The amounts of acetone produced by a given organism vary considerably with the nature of the medium. W. G.

Acclimatisation of Yeast to Ammonium Fluoride and its Reversion in Wort. Ellis I. Fulmer (*J. Physical Chem.*, 1921, **25**, 455—472).—The toxicity of aqueous and aqueous alcoholic solutions of ammonium fluoride toward yeast has been investigated. It is shown that alcohol increases the toxicity. In acclimatising yeast to ammonium fluoride it is not necessary to commence with low concentrations (Effront's stepping-up method); the cells may be planted at once in the more concentrated solutions of fluoride and wort and will grow if left long enough. The time elapsing between seeding and active fermentation depends on the method of preparing the wort, on the character of the individual yeast-cells, and on the previous history of the culture. Yeasts acclimatised to a given concentration of fluoride by different routes behave differently towards more concentrated fluoride solutions. If the logarithm of the interval between seeding and active fermentation be plotted against concentration, for various yeasts, acclimatised and unacclimatised, the experimental data fall on straight lines radiating from a point corresponding with about 7—8 grams of ammonium fluoride per litre. The highest concentration in which yeast will grow is about 7 grams per litre. Yeast acclimatised to ammonium fluoride is more resistant to phenol than is normal yeast. Acclimatised yeast may be grown on fluoride free wort agar for twelve days or in fluoride-free wort for one hundred and ninety hours without completely reverting to normal. When yeast is planted in wort containing ammonium fluoride, a proportion of the cells die, that is, they will not reproduce on fluoride-free wort agar. The number of living cells decreases, passes through a minimum, which may be less than 1 in 1200 of those originally present, and then increases. Selection plays a part in the acclimatisation. Measurements of the rate of reproduction of yeast in wort with and without ammonium fluoride show that the cells which are not killed outright undergo a period of paralysis, after which they reproduce, giving rise to fluoride resistant cells. Adaptation plays a part in the acclimatisation. The maximum value for the duration of paralysis may be calculated from the experimental results. J. F. S.

Catalytic Processes of Physiological Importance Effected by Light. Kurt Noack (*Zeitsch. Bot.*, 1920, **12**, 273—349).—The chemical action of light on cells occurs through the agency of substances which transform light energy into chemical energy. Two groups of such catalysts are recognised: fluorescent organic compounds, and salts of certain heavy metals. Both serve as carriers of oxygen. From experiments on chromogens and many plants the author concludes that the fluorescent organic compounds

act by the formation of peroxides. Their action is stopped by sodium sulphite. The salts of the heavy metals act by change in the valency of the metal. CHEMICAL ABSTRACTS.

The Relation of the Hydrogen-ion Concentration of Nutrient Solutions to Growth and Chlorosis of Wheat Plants. A. G. McCALL and J. R. HAAG (*Soil Sci.*, 1921, **12**, 69—77).—Wheat plants were grown for two months on sand cultures supplied with four different nutrient solutions, each of which was modified in such a way as to have three distinctly different p_H values without materially altering the solutions with respect to the concentrations of the six essential ions. The results indicate that hydrogen-ion concentration exerted a very marked influence on the rate of growth and was also an important factor in the control of chlorosis. There was some evidence that the plants grown in solutions having p_H values ranging from 4·02 to 7·0 were suffering from the lack of available iron or from faulty metabolism resulting from the immobility of the iron within the plants. W. G.

The Relation of Sulphates to Plant Growth and Composition. H. G. MILLER (*J. Agric. Res.*, 1921, **22**, 101—110).—Nodule production and nitrogen assimilation of legumes were stimulated by the addition of sulphates. On the other hand, the supply of nitrate available to the plant appeared to limit the amount of sulphur assimilated. In the case of rape, no direct relationship between nitrogen and sulphur assimilation was observed. [See also *J. Soc. Chem. Ind.*, 1921, 861A.] A. G. P.

Vegetable Assimilation and Respiration. XIV. Assimilation by Submerged Plants in Dilute Solutions of Bicarbonates and of Acids : an Improved Bubble-counting Technique. A. J. WILMOTT (*Proc. Roy. Soc.*, 1921, [*B*], **92**, 304—327).—Disturbances in bubbling experiments are eliminated by using a glass bubbler and a bubbling cup. By means of this apparatus it is shown, (1) that the increased rate of bubbling by submerged water plants when placed in acid solution is due to the decomposition of calcium carbonate deposited on their surface, (2) that the rate of assimilation of carbon dioxide from sodium hydrogen carbonate solution corresponds with the calculated concentration of carbon dioxide, the conclusion being drawn that plants do not possess the power of decomposing sodium hydrogen carbonate.

E. S.

First Products of the Chlorophyll Assimilation of Carbon. E. ROUGE (*Schweiz. Apoth. Zeit.*, 1921, **59**, 157—161, 175—178).—The history of the problem of carbon dioxide absorption by plants is reviewed. A test for glycollaldehyde consists in the preparation of the p-*nitrophenylhydrazone*, reddish-brown needles, m. p. 177° (decomp.), and soluble in alcoholic potassium hydroxide with a blue colour. By this method, glycollaldehyde has been identified in various green leaves; the method of its formation is considered theoretically. CHEMICAL ABSTRACTS.

Hemicellulases in Resting Seeds and their Supposed Occurrence in Higher Animals. AUGUST RIPPEL (*Landw. Versuchs.-Stat.*, 1921, **97**, 179—193).—It has been suggested that the digestion of hemicelluloses by higher animals is due to the occurrence of appropriate enzymes in the alimentary tract. Working with seeds of *Lupinus angustifolius*, L., the author shows that an intensive autolysis of the water-soluble hemicelluloses takes place with formation of sugar; there is also a further autolysis of hemicelluloses which are not immediately soluble in water. The enzyme concerned in the reaction is specific and present as such, is not destroyed by heating at 105°, and is distributed throughout the seed. Similar autolytic actions were observed in the case of *Galium aparine*, L., and *Asparagus officinalis*, L. The occurrence of hemicellulases in seeds is a sufficient explanation of the digestion of hemicelluloses by animals. G. W. R.

Incrustive Substance of Plants. I. Method of Preparing Plant-tissue Substances in the Pure Condition. I. ERICH SCHMIDT and ERICH GRAUMANN (*Ber.*, 1921, **54**, [*B*], 1860—1873).—The complete removal of incrustive substances from plants, for example, lignin from wood, has only been possible previously by the use of reagents which also attack the polysaccharide. It is now shown that unchanged carbohydrates, completely free from incrustive substance, can be readily prepared by the use of aqueous solutions of chlorine dioxide which have no effect on cellulose, mercerised cellulose, oxycellulose, mannan, xylan, starch, and fungus-cellulose. The stability of the carbohydrates towards chlorine dioxide is confirmed further by the observation that their components, dextrose, mannose, galactose, lævulose, xylose, arabinose, maltose, and glucosamine hydrochloride do not react with solutions of the gas. The presence of small amounts of incrustive substance is readily detected by the consumption of chlorine dioxide, and in consequence of this behaviour it is easily possible to estimate quantitatively the percentage of incrustive and tissue substance in portions of plants. In this manner pine (*Pinus silvestris*, L.) is found to contain 63·28% of tissue substance and 36·72% of lignin, whereas Willstätter and Zechmeister found only 27·35% of the latter. The consumption of chlorine dioxide is small amounting, in the case of pine wood, to 13·50% of the weight of the wood.

With the help of chlorine dioxide it has been found possible to establish the presence of polysaccharides in lignin; the hydrolysis of these only becomes possible after the destruction of the components of lignin which are attacked by solutions of the gas.

The preparation of a saturated aqueous solution of chlorine dioxide from potassium chlorate and oxalic acid is described fully, as are also the methods of estimating chlorine dioxide in aqueous solution. The sensitiveness of the carbohydrates or incrustive substance is measured by allowing them to remain in contact with the *N*/20- or *N*/5-solution of the gas for a period of twenty-four hours at the atmospheric temperature (a little acid is added if

necessary to overcome possible alkalinity of the material) and estimation of the concentration of the solution before and after this treatment. For the removal of incrustive substance, the wood shavings are extracted with alcohol–benzene mixture to remove the greater part of the resin, finely ground, and again extracted. The dry wood (100 grams) is covered with *N*/5-chlorine dioxide solution (2—3 litres) in a stoppered, brown glass bottle and allowed to remain in diffused light and with occasional agitation for about twenty-four hours at the atmospheric temperature. The residue is filtered and treated successively with water, 2% aqueous sodium sulphite solution, and hot water, and the processes are repeated until the material is free from incrustive substance (generally three to eight times). The preparation of incrustive-free xylan and mannan is described in detail; in each case, it is noticeable that the action of sodium hydroxide solution causes changes in the respective molecules which lead to the presence of groups attackable by chlorine dioxide. H. W.

Hydrocyanic Acid in Sudan Grass. C. O. SWANSON (*J. Agric. Res.*, 1921, **22**, 125—138).—Hydrocyanic acid was obtained from the leaves of Sudan grass by digesting the macerated material with water at room temperature for six hours. The free acid does not occur in the green plant as such, but is produced by the action of enzymes during maceration and also during severe wilting of the plant. [See also *J. Soc. Chem. Ind.*, 1921, Dec.] A. G. P.

Carbohydrates of the Root of the Cat-tail (*Typha latifolia*). ZALIA JENCKS (*Proc. Soc. Expt. Biol. Med.*, 1919, **17**, 45—46).—The root of the cat-tail, recently recommended as a valuable food for man, contains 81% of carbohydrates. The most abundant carbohydrate of the root gives a blue colour with iodine, forms a characteristic paste with hot water, is readily digested (in contrast with inulin) by saliva, and yields on hydrolysis a dextrorotatory solution from which an osazone, identical with glucosazone, was prepared. It thus corresponds with starch. The "flour" was found to contain 56·8% of carbohydrate. Mice were fed for a week on otherwise adequate diets containing 30% of the "flour" without any evident untoward results. The animals gained in weight on the ration. CHEMICAL ABSTRACTS.

The Influence of certain Fertiliser Salts on the Growth and Nitrogen Content of some Legumes. ALEXANDER MACTAGGART (*Soil Sci.*, 1921, **11**, 435—455).—Nitrogen was applied in the form of dried blood, phosphorus as disodium hydrogen phosphate, potassium as potassium chloride, and sulphur as calcium sulphate, and all the soils received a dressing of calcium carbonate. The fertilisers were applied singly and in groups, and the crops were lucerne, Canadian field peas, and soja beans. Of all the four fertiliser elements phosphorus showed the most marked effect whether applied singly or with other fertilisers. It increased the dry matter, total nitrogen, and, to a lesser extent, the percentage of nitrogen

in all three legumes. Nitrogen had very little, if any, beneficial effect on the legumes. The action of potassium was not uniform on the three crops examined. Sulphur, in the form of gypsum, benefited to some extent the lucerne crop, but had no effect on the peas or beans. There appeared to be some correlation between the plant dry matter produced and subsequent soil nitrification.

W. G.

The Effect of Soil Temperature on the Development of Nodules on the Roots of certain Legumes. F. R. JONES (*J. Agric. Res.*, 1921, **22**, 17—31).—Maximum nodule production occurs at about 24° in all plants examined, and is in no way connected with maximum growth of the plant. Usually conditions favourable to nodule production bring about high nitrogen content in the foliage.

A. G. P.

Influence of Temperature on the Absorbent Properties of Soils. STOQUER (*Compt. rend.*, 1921, **173**, 731—733).—Four types of soils were used, 100 grams of the soil being shaken with 250 c.c. of ammonium sulphate solution at the given temperature for one hour, and the ammonia remaining in the solution estimated by distillation. The temperatures used were 0°, 16°, 35°, and 55°. In all cases, the absorption diminished as the temperature increased, and with two types of soil there was a negative absorption when a 0·002% solution of ammonium sulphate was used at temperatures above 0°.

W. G.

Concentration and Composition of the Soil Solution. F. W. PARKER (*Soil Sci.*, 1921, **12**, 209—232).—The author discusses the different methods which have been used for obtaining the soil solution in an unaltered state. A description is given of a displacement method in which ethyl alcohol is used as the displacing liquid. The constancy of composition of the displaced solution was checked by freezing-point determinations which also served to indicate the appearance of the displacing liquid in the percolate. The concentration of the soil solution was found to be inversely proportional to the amount of moisture originally present in the soil. A study of the freezing points of soils containing varying amounts of moisture showed that the depression gives no measure of the concentration of the soil solution at ordinary moisture contents. In soils nearly saturated with water, freezing-point depressions may give some indication as to the concentration of the soil solution. The discrepancies at low moisture contents are due to the fact that the water is present in the form of capillary films, and not to its removal from the rôle of solvent, as has been assumed by other workers.

G. W. R.

Effect of Salt Solutions on the Soil. O. NOLTE (*Landw. Versuchs.-Stat.*, 1921, **98**, 135—153).—A continuation of earlier work (A., 1917, i, 621) on the reaction between the soil and salt solutions. The reaction of a soluble salt with soil is reflected in its

effect on the permeability. Neutral salts and hydrogen ions favour flocculation whilst hydroxyl ions favour deflocculation. The effect of any salt on soil structure is thus determined by its reaction with the soil constituents. The effect of different solutions on soil structure was studied in a special apparatus, whereby the rate of percolation through a soil column could be followed over long periods. The continued passage of distilled water leads to a steady decrease in permeability consequent on the washing out of soluble salts. The effect of each solution was studied by allowing it to percolate for three weeks after a preliminary period of three to four weeks in which distilled water was passed through. The percolating liquid was collected daily and analysed weekly as a composite sample. The results are set out in graphic form and should be consulted in the original paper. They are in general agreement with theoretical considerations. G. W. R.

The Reaction of Potassium Ammonium Nitrate with Soil. NIKOLAUS KEMPF (*Landw. Versuchs.-Stat.*, 1921, **97**, 195—217).—The absorption of the ions of salts by the soil was studied, using potassium ammonium nitrate (Kaliammoniaksalpeter), a new fertiliser prepared from synthetic ammonium nitrate and "40% potash salt." As a preliminary experiment, a sample of the soil under experiment was extracted with water in order to discover its content in soluble salts which might be presumed to take part in absorption equilibria. Known weights of the soil were uniformly moistened with known volumes of a solution of the fertiliser and after remaining for varying times the soil solution was obtained by adding excess of water and filtering. The amount of absorption of each ion was determined by estimating the amount in solution and subtracting from the amount added, making allowance for the water soluble material originally present in the soil. The univalent ions, potassium, sodium, and ammonium are all absorbed to some extent by the soil and approximately equivalent amounts of the bivalent ions, calcium and magnesium are displaced. While the amount of absorption of sodium decreases, the absorption of potassium and ammonium increases with time. The approximate equivalence of the univalent ions absorbed with the bivalent ions displaced into solution holds throughout. A small absorption of nitrate takes place. The absorption of chloride lies within the limits of experimental error. The behaviour of the sulphate ion is irregular and the amount in solution decreases after long keeping, probably owing to the formation of calcium sulphate. Absorption is almost instantaneous, and the further changes above described take place slowly. G. W. R.

Solubility of Anions in Alkali Soils. W. P. KELLEY and S. M. BROWN (*Soil Sci.*, 1921, **12**, 261—285).—The absorption of salts by alkali soils has been studied by determining the amount of different anions extracted by water under varying conditions of time of shaking, and ratio of water to soil. Experiments were also made in which soils were extracted with successive portions

of water. Whilst the amount of total solids extracted increases with time of shaking, no consistent variation was found in the case of any of the anions, and it is concluded that approximate equilibrium is attained at the end of one hour. Variation in the ratio of water to soil was without effect on the amount of chloride and nitrate extracted. In the case of carbonate and hydrogen carbonate, however, two of the three soils studied gave up increasing amounts with larger volumes of extracting water. A slight increase in the amount of sulphate extracted was also observed with increase of the ratio of water to soil. In the case of chloride, nitrate, and sulphate, a very large proportion of the total amount was extracted by the first treatment with water; in the case of the normal and hydrogen carbonate, however, greater amounts were dissolved by the second extraction. The conclusion is drawn that alkaline salts are either adsorbed or held in loose combination to a greater degree than neutral salts. G. W. R.

The Effect of Organic Matter on Soil Reaction. R. E. STEPHENSON (*Soil Sci.*, 1921, **12**, 145—162).—A study is made of the effect of ploughing in crop residues, etc., on the soil reaction. In general, the lime requirement of the soil (Tacke method) is reduced by this treatment until nitrification begins. Determinations of the H-ion concentration show that true acidity also is decreased. Highly organic and clay soils show a marked capacity for buffering, a property which is considerably limited in sands. Sulphuric acid and physiologically acid salts tend to raise the H-ion concentration, but citric acid does not. Ammonium sulphate causes a greater increase in acidity than does its nitrogen equivalent in albumin; but less than the equivalent in mixed nitric and sulphuric acids. A value of $p_H=8$ seems to be about the limit of alkalinity produced by limestone. [See also *J. Soc. Chem. Ind.*, 1921, 860A.] A. G. P.

Soil Acidity and Bacterial Activity. R. E. STEPHENSON (*Soil Sci.*, 1921, **12**, 79—132).—The work described is a continuation of that in a former paper [*ibid.*, 1918, **6**, 413—439], and deals with the effects on soil reaction and bacterial activity in soils of various organic nitrogenous manures, both in the presence and absence of lime. The lime requirement was in no case increased by organic treatment, except during the rapid production of nitrates. Lime stimulates nitrification, whereas ammonification was greater in unlimed soils. The latter is due to the lower activity of nitrifying organisms in this case. The total ammonia plus nitrates is greater in unlimed than in limed soil treated with organic material. Dung and timothy hay reduced ammonification and nitrification below that of untreated soil. Green manures were more rapidly attacked than dried material.

In practically all cases unlimed soils had a greater non-protein nitrogen content than the limed. Generally speaking, the essential soil organisms are active in soils of at least moderate acidity.

A. G. P.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Molecular Refraction Coefficient, its Additivity Character and its Use for Determining Constitution. II. The Calculation of Refractive Indices of Aromatic Hydrocarbons. FRITZ EISENLOHR (*Ber.*, 1920, **53**, [*B*], 2053—2063).—In a previous paper (A., 1920, ii, 717) it was pointed out that the "molecular coefficient of refraction," $M \times n_D^{20}$, is more sensitive to constitutive changes in the molecule than the generally employed "molecular refraction." A study of the aromatic hydrocarbons of the benzene series shows that the value of the coefficient depends on the relative positions of the substituting alkyl groups in the ring. The observed values exceed those calculated from the atomic values of the constituent atoms, after allowance has been made for ring formation, by an amount which is termed the *E* value. When the *E* values associated with a limited number of groupings are known, for example, two methyl groups in ortho-, meta-, or para-positions, three methyl groups in 1:2:4-positions, etc., it becomes possible to calculate the *E* value, and consequently the molecular coefficient of refraction and refractive index, of any hydrocarbon of the series. A number of typical examples of such calculations are given. E. H. R.

The Dispersion of the Refraction of Hydrocarbons. E. DARMOIS (*Compt. rend.*, 1920, **171**, 952—955).—The specific dispersion of a substance is defined as being the ratio $\Delta n/d$, where

Δn is the difference in the refractive indices for H_α and H_γ, and d is the density at the same temperature. The value of this ratio is apparently constant within one or two units for each type of hydrocarbon, and thus serves to distinguish between saturated, unsaturated, and benzenoid hydrocarbons. The value of $\Delta n/d$ in the case of unsaturated hydrocarbons increases with the number of ethenoid linkings in the molecule. W. G.

Effect of Concentration on the Spectra of Luminous Gases. T. R. MERTON (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 255—260).—There are many cases in which the relative intensities of the lines in a mixture of two gases are altered by the inclusion of a condenser and spark-gap in the electrical circuit. The phenomena have been attributed to changes in the electrical conditions, but experiments described indicate that the ultimate cause may be an alteration of the relative proportions of the two gases in the capillary of the discharge tube.

The broadening and enhancement of certain lines in the case of sodium and lithium when one element is added to the other have been referred to temporary association of atoms of the two elements, but experiments with these elements seem to exclude this explanation. J. R. P.

Excitation of the Spectrum of Helium. K. T. COMPTON and E. G. LILLY (*Astrophys. J.*, 1920, **52**, 1—7).—A discussion of the minimal voltage required for the excitation of the different components of the helium spectrum. Radiation is excited by a stream of electrons emitted by an incandescent tungsten wire, and drawn through the gas to a nickel disk anode by a field which can be varied between 0 and 120 volts. Observing proper precautions, it was possible to obtain a brilliant helium spectrum free from all impurities, including hydrogen, neon, and the vapours of mercury and water. The band spectrum, very intense under these conditions, is thus conclusively shown to belong to helium. The band spectrum and the singlet and doublet series appear simultaneously at 25·5 volts with low pressures and at voltages as low as 20 with higher pressures and current densities, pressures up to 24 mm. being used. The corresponding voltages for the enhanced line at λ 4686 Å. are 80 and 55 volts. These results indicate that the minimal voltages for the excitation of the normal helium atom by a single electronic impact are 25·5 and 80 volts, but when multiple impacts assist, the corresponding voltages may drop to 20 and 55, but no lower. The last value agrees with that predicted by the Bohr theory for the energy necessary to displace the second electron from a singly ionised helium atom. The fact that after striking the arc it can be maintained on as little as 8 volts by using high currents indicates that in an intense discharge a large proportion of the atoms is in an abnormal state, and therefore requires less energy for excitation. The relative intensities of the different components of the spectrum change with varying conditions. As the voltage is increased, the sharp, subordinate

series becomes relatively weaker. As the pressure is increased, the band spectrum becomes stronger and the enhanced line weaker. The former is stronger near the cathode, the latter near the anode. The addition of a trace of neon caused the neon lines λλ 5331 Å. and 5431 Å. to appear with remarkable intensity.

CHEMICAL ABSTRACTS.

A Band Spectrum from Mercury Vapour. C. D. CHILD (*Science*, 1920, **52**, 248—249).—A continuous spectrum is produced by mercury vapour which is condensing by means of a low-voltage discharge obtained from a transformer of a Wimshurst machine. The spectrum is independent of the purity of the mercury or of the material of the electrode or glass. The glow lasts about 0·001 second, and the radiators do not bear charges.

CHEMICAL ABSTRACTS.

Spark Spectra of Mercury, Copper, Zinc, and Thallium in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1920, **171**, 909—912).—The spark spectrum of mercury between λ 1650 and 1400 is given, and thirty-six new lines are reported. The spectrum for copper is given between λ=1790 and 1543, and seventeen new lines are recorded. The spectrum of copper is terminated by a characteristic group of four lines at λ=1552·3, 1550·2, 1548·0, and 1543·0. The spark spectrum of zinc between λ=1850 and 1445 shows twelve new lines. The spark spectrum of thallium between λ=1840 and 1477 is given, and contains thirteen new lines.

W. G.

Extension of the Ultra-violet Spectrum. R. A. MILLIKAN (*Astrophys. J.*, 1920, **52**, 47—64).—The extreme ultra-violet spectrum has been extended to λ 202 Å. The source was a high-potential spark, discharged in high vacuum. The vacuum was maintained at less than 10^{-4} mm. by means of a mercury diffusion pump, operated continuously. The current was furnished by the discharge of Leyden jars at a potential of several thousand volts. In such high vacua it was necessary to keep the electrodes at a distance of 0·2 mm. or less, in order to spark between metals, though carbon electrodes could be separated by 1 or 2 mm. The spectra were photographed by means of a concave grating of 83 cm. focal length. The grating was ruled with the exacting requirements of this investigation in view. The spectra of carbon, zinc, iron, silver, and nickel have been extended to λλ 360·5, 317·3, 271·6, 260, and 202, respectively. Excellent illustrations of the extreme ultra-violet vacuum spark spectra of carbon, zinc, iron, and nickel are shown. Evidence is presented for believing that the whole spectrum which the carbon atom is able to emit, up to and including its *X*-radiations of the so-called *L*-series, has now been obtained. Various formulæ for predicting the position of this series are discussed. Previously, no lines of the *L*-series of any element with an atomic number less than 30 had been identified. The conclusion is drawn that high-potential vacuum sparks are

sources of X-rays; in fact, X-rays were observed in these sparks by the usual means. CHEMICAL ABSTRACTS.

Wave-lengths longer than 5500 Å. in the Arc Spectra of Seven Elements. C. C. KIESS and W. F. MEGGERS (*Bur. Standards, Bull.*, 1920, **16**, 51—73; *Sci. Paper* **272**).—The concave grating spectrograph of the Bureau of Standards was used in photographing the yellow, red, and infra-red arc spectra of titanium, vanadium, chromium, manganese, molybdenum, tungsten, and uranium. The photographs were made on plates sensitised to the red and infra-red rays with pinacyanol and dicyanin. The wave-lengths of about 200 lines in the arc spectrum of titanium were measured between the limits 5500 Å. and 9743 Å., 250 lines to 9522 Å. in vanadium, 130 lines to 9734 Å. in chromium, 193 lines to 9576 Å. in manganese, 545 lines to 9721 Å. in molybdenum, 478 lines to 9159 Å. in tungsten, and 680 lines to 9530 Å. in uranium. Many of the measurements represent wave-lengths of heads of bands which are especially prominent in the spectra of titanium, vanadium, and chromium. Impurity lines were eliminated from the tables so far as known, those not identified being brought together in a separate table. Lines the wave-lengths of which agree with those in the series spectrum of oxygen were repeatedly observed in the spectra of arcs in air. Frequency differences which are suspected of being constant were found in each of the spectra. CHEMICAL ABSTRACTS.

Elements in the Sun. (Paper B.) MEGH NAD SAHA (*Phil. Mag.*, 1920, [vi], **40**, 808—824).—No evidence of the existence of the following elements in the sun has been obtained: rubidium, cæsium, nitrogen, phosphorus, boron, antimony, bismuth, arsenic, sulphur, selenium, thallium, praseodymium. Doubtful indications of the following have been obtained: radium, elements of the inert group, except helium, osmium, iridium, platinum, ruthenium, tantalum, thorium, tungsten, uranium. The following are represented by faint lines in the Fraunhofer spectrum: potassium, copper, silver, cadmium, zinc, tin, lead, and germanium. Chlorine, bromine, iodine, fluorine, and tellurium have not been investigated.

It is usually assumed that elements of which no indications are found in the Fraunhofer or flash spectra are totally absent from the sun. The view is urged, however, that the varying records of different elements in the Fraunhofer spectrum may be regarded as arising from the varying response of these elements to the stimulus arising in the sun. This stimulus is the same for all elements, namely, a temperature of 7500° abs., but, owing to differences in internal structure, elements will respond in different degrees to this stimulus. This theory is examined from the point of view of the ionisation potentials of the various elements. J. R. P.

Absorption of some Diatomic Gases in the near Infra-red. ELMER S. IMES (*Astrophys. J.*, 1919, **50**, 251—276).—The importance of the study of absorption bands of gases in the near

infra-red arises, first, from the information given with regard to the structure and mechanics of the molecule, including inferences as to atomic structure, and, secondly, in the new application and test of the quantum theory extended to the rotational energy of molecules. A summary of the theory and previous work is given. More extended and more accurate data are obtained of the absorption bands of hydrogen fluoride, chloride, and bromide. Tables and curves are presented showing the bands of hydrogen chloride at 1·76 μ and 3·46 μ in great detail, and giving for hydrogen bromide a similar band at 3·9 μ resolved into its quantum lines, and, for hydrogen fluoride, a band at 2·5 μ, which has not been studied before. The positions of the absorption maxima are determined with an accuracy of several Ångström units. From experimental results, the lengths and moments of inertia of these three molecules are computed: $l \times 10^8 = 0{\cdot}94$, 1·28, and 1·42, and $I \times 10^{40} = 1{\cdot}37$, 2·64, and 3·27 for hydrogen fluoride, chloride, and bromide respectively. Instead of perfect symmetry of maxima, that is, arithmetical progression in the frequencies of the maxima, there is a gradual increase in the frequency difference between two adjacent maxima in the infra-red in the direction of longer wave-length, indicating that the vibration frequency of the atoms in the molecule is dependent on the rotation frequency of the molecule. Kemble (A., 1917, ii, 402) advanced the theory that if the amplitude of vibration of the molecule is that required by even a single quantum, the infra-red absorption bands should be accompanied by faint harmonics. Doublets agreeing approximately with the predictions were previously found, and inexact verification was explained by errors in dispersion curves. Only one harmonic, in the case of hydrogen chloride, was observed in this work, the ratio being 1·963 : 1 instead of the expected 2 : 1, that is, the harmonic is 0·033 μ further in the infra-red than the predicted position.

CHEMICAL ABSTRACTS.

Spectro-chemical Study of the Allyl- and Methylalylll*cyclo*-hexan-2-ones. R. CORNUBERT (*Compt. rend.*, 1920, **171**, 919—921, 1060—1062).—The values of the refractive indices, n^{24}, and the densities, D_4^{24}, of the α-allyl derivatives of *cyclo*hexanone, and of α-, β-, and γ-methyl*cyclo*hexanones, are given. For each series of ketones there is an alternation in the variation of the density with respect to the number of alkyl groups in the α-position. In every case, the ketone with three alkyl groups only shows a slight increase in its refractive index over that of the next lower member. The formation of a "double" group of the type CRR: causes a depression of the molecular refraction, whilst the formation of a "single" group of the type CHR: is without appreciable influence on its value.

Starting with 1 : 1 : 3 : 3-tetramethyl*cyclo*hexan-2-one, and replacing the methyl groups one at a time by an allyl group, the effect on the molecular refraction has been observed. The results show the absence of any influence due to dimethyl groups, but the

marked effect due to diallyl groups. The data given support Auwers' theory on the influence of double groups on the value of the molecular refraction. W. G.

Colour and Chemical Constitution. X. A General Numerical Solution of the Colour-Constitution Problem. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1920, **8**, 303—311. Compare A., 1920, ii, 573).—It is suggested that the influence of various substituents on the wave-lengths of absorption bands of dyes of the triphenylmethane series is represented by definite factors, which are derived as follows. That for *p*-OH, for example, is obtained from the ratio $\lambda_{aurin}/\lambda_{benzaurine}=0{\cdot}9657$. Similarly, values (in parenthesis) are derived for *p*-NH_2 (0·972), *N*-methyl (1·0245) [giving NHMe (0·9965) and NMe_2 (1·021)], *N*-ethyl (1·023); for the phthaleins, *o*-CO_2H (1·002), *o*-Me, -Et, $C_3H_7^{\beta}$, -Cl -Br, -I (1·013 ± 0·001), γ-OMe (0·973), *o*-OH (1·030), *o*-OMe (1·037), α-SO_3H (1·018). Values of a more tentative character, owing to lack of data for purposes of control, are also given for α-Br (1·027), β-Br (1·022), γ-Br (0·975), β-CO_2H (1·012), γ-CO_2H (0·995), β-SO_3H (1·01), γ-SO_3H (1·027), ε-SO_3H (1·010), α-NH_2 (1·022), *C*-Ph (1·026). The colour factor for four methyl groups appears also to apply to the thiophenazine dyes, since $\lambda_{methylene\text{-}blue}/\lambda_{thionine}=\lambda_{malachite\text{-}green}/\lambda_{Doebner's\text{-}violet}$. The factor for replacement of -CH: by -N: (triphenylmethane ⟶ indamine series) is about 1·20. J. K.

The Light Diffused by Argon. LORD RAYLEIGH (*Compt. rend.*, 1920, **171**, 1002).—In connexion with a recent paper by Cabannes (A., 1920, ii, 722), the author draws attention to his own revised value of 99·1% for the degree of polarisation of the light diffused by argon (compare *ibid.*, ii, 574). W. G.

Dependence of Optical Rotatory Power on Chemical Constitution. III. 1 : 4-Naphthylenebisiminocamphor. BAWA KARTAR SINGH and MAHAN SINGH (T., 1920, **117**, 1599—1601).

Dependence of Electrical Double Refraction on Temperature. NIKOLAUS LYON and FRITZ WOLFRAM (*Ann. Physik*, 1920, [iv], **63**, 739—752).—The dependence of the electrical double refraction of ethyl ether, carbon disulphide, and toluene was determined for various temperatures between 18° and −78·5°, and the results compared with the theories of Langevin and of Born. The agreement with the theory of Langevin was good, but the values calculated by Born's formula were, without exception, higher than the observed results. J. R. P.

The *K* characteristic Absorption Frequencies for the Chemical Elements Magnesium to Chromium. HUGO FRICKE (*Physical Rev.*, 1920, **16**, 202—215).—Photographs showing the discontinuities in the *X*-ray absorption bands correspond-

ing with the *K*-series of the elements from magnesium to chromium were studied. The wave-lengths of the more important parts are tabulated, and indicate considerable complexity.

CHEMICAL ABSTRACTS.

The Charge on the Atomic Nucleus and the Law of Force. J. CHADWICK (*Phil. Mag.*, 1920, [vi], **40**, 734—746).—The charges on the nuclei of three atoms have been measured by a direct method depending on the scattering of α-particles. The values found were: platinum 77·4, silver 46·3, copper 29·3, in fundamental units of charge. The atomic numbers of these elements are 78, 47, and 29, respectively.

The particles were scattered by causing them to pass through thin metal foil in the form of an annular ring subtending a fairly wide cone at the source. Both the scattered and direct particles were counted on the same zinc sulphide screen under the same conditions. In this way, the counting was more convenient, and a greater number of particles could be counted than with former methods.

The law of force around the platinum nucleus was tested by measuring the dependence of scattering on the velocity of the α-particle. The result showed that the inverse square law holds accurately in the region concerned, namely, about 10^{-11} cm. from the nucleus.

The results obtained, together with those of other experimenters, show that, measured from any point in the region between 3×10^{-12} cm. and 10^{-10} cm. from the nucleus of a heavy atom, like platinum, the charge is equal to the atomic number, and the law of force is the inverse square. It may therefore be concluded that no electrons are present in the region between the nucleus and the *K* ring.

J. R. P.

Cathode Fall in Neon. ARTHUR H. COMPTON and C. C. VAN VOORHIS (*Physical Rev.*, 1920, **15**, 492—497).—Measurements are made of the potential difference between the cathode and the beginning of the positive column when a discharge is passed through pure neon, using a number of different metals as cathode. The "normal cathode fall," or potential difference, between the cathode and the cathode glow for normal current is also determined for several metals. It is found that for normal current the potential difference between the cathode and the positive column is very nearly proportional to the potential differences between the cathode and the cathode glow when different metals are used as cathode. The values in volts of the normal cathode fall in neon were found to be: with Pt cathode 152, W 125, Tl 125, Al 120, Mo 115, Mg 94, Ca 86, Na 75, and K 68. These values are in the order, as far as available data go, of the contact potential series, and are consistently slightly lower than the corresponding values in helium.

CHEMICAL ABSTRACTS.

The Independent Origin of Actinium. ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1920, **42**, 2205—2208).—Piccard's assumption (A., 1918, ii, 6) that the actinium series is derived neither from uranium-*I* nor from uranium-*II* does not require, as supposed by Soddy (A., 1918, ii, 211), the identity of the periods of the first and third. The relation of the uranium, actinium, and thorium series becomes more symmetrical if a hypothetical isotope of proto-actinium (ekatantalum or uranium-*Z*) is assumed as the parent of actino-uranium by a β-ray transformation. This element and actino-uranium have assigned to them an atomic weight 235, corresponding with proto-actinium 231, actinium 227, and actinium lead 207. The last value agrees well with Hönigschmid's value of 206·05 for the atomic weight of uranium lead containing approximately 3% of actinium lead. J. R. P.

Rate of Decay of Actinium and the Transformation Relationships of the Actinium Series. STEFAN MEYER (*Wien. Anzeiger*, 1920, 133; from *Chem. Zentr.*, 1920, iii, 761). —The half-life period of actinium is calculated to be about sixteen and a-half years, and the transformation ratio of the actinium to the uranium–radium family to be 4%. H. W.

Resonance Potentials and Low-voltage Arcs for Metals of the Second Group of the Periodic Table. F. L. MOHLER, PAUL D. FOOTE, and W. F. MEGGERS (*J. Opt. Soc. Amer.*, 1920, **4**, 364—370).—A four-electrode tube was used, in which a hot wire cathode was surrounded by two cylindrical grids and a plate. The grids, of which one is close to the cathode and the other close to the plate, are maintained at the same potential by a metallic contact; a variable accelerating field for electrons is used between the cathode and inner grid, and the current reaching the plate against a small retarding field between the outer grid and plate is measured. The ionisation and resonance potentials, in volts, were found to be: zinc, 9·3, 4·18, 5·65; cadmium, 9·0, 3·95, 5·35; mercury, 10·2, 4·76, 6·45; magnesium, 8·0, 2·65, 4·42; calcium, 6·01, 1·90, 2·85. In all cases, the values are compared with the theoretical values. Some general conclusions are drawn for electron impacts with molecules of metals of the second group. J. R. P.

The Nature of the Ions produced by Phosphorus. J. A. MCCLELLAND and P. J. NOLAN (*Proc. Roy. Irish Acad.*, 1919, **35**, [*A*], 1—12).—The work was undertaken to see if any of the groups of ions of various characteristic mobilities, obtained by bubbling air through mercury and through alcohol, were present in the ionisation produced by drawing air over phosphorus. Under various conditions, fourteen different types of ions have been found in this air, with mobilities, in a field of 1 volt/cm., of 0·22, 0·092, 0·053, 0·028, 0·018, 0·0074, 0·0041, 0·0024, 0·0012, 0·00064, 0·00031, 0·00015, 0·000085, and 0·000053 cm./sec. Some of the more mobile ions are only obtained in dried air with a short

interval between formation and measurement, and some of the slower ions only in undried air with a long time interval. Both positive and negative ions in each group are present in similar quantity, and the mobility does not change with time. All the ions produced by phosphorus, except the two slowest, are observed in bubbling experiments, which points to the conclusion that they are largely composed of water. Different nuclei in different cases appear to act as the starting point of the ion, but the growth system seems to be the same in the case of phosphorus ionisation as in the case of bubbling. F. S.

Behaviour of Electrolytic Ions in Solid Substances. II. Dissociation Relationships in Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. Elektrochem.*, 1920, **26**, 472—480. Compare A., 1919, ii, 490).—The electrolytic conductivity and the volume change of permutite mixtures have been determined for the base exchange, potassium–cadmium, potassium–lead, lithium–cadmium, and potassium–chromium. The observed values, and those calculated on the basis of theoretical considerations, are in very good agreement, so that the author is enabled to make the following statements. The dissociation relationships of potassium permutite and lithium permutite are approximately the same, just as are those of similar salts in aqueous solution, and they change in the same way on dilution. The laws governing the influence of two salts with the same anion on the dissociation are true for solid permutite, in exactly the same way as for salts in solution. By the continuous replacement of the cation of a strongly dissociated permutite by that of a weakly dissociated permutite, the mobility of the former is reduced, since the undissociated, and therefore stationary, cation of the second permutite reduces the space available for the movement of the first cation. Permutite takes up a volume, determined by every type of cation in it, since each pure permutite has a different molecular volume, which depends on the ion volumes of the base. The molecular volume changes with base interchange proportionally with the amount of interchange as long as the amount of water of crystallisation remains constant. This will also affect the space available for the migration of the cation. All permutites examined up to the present contain $5H_2O$, except chromium permutite, and this contains $13H_2O$. These enter into the interior of the molecule, which is thereby considerably loosened, so that the mobility of the chromium cation is very much increased, and in the case of pure chromium permutite has a value of the same order as that of the chromium ion in aqueous solution. In those cases where the base interchange brings about a very small electrolytic conductivity, the interchange is very slow, so that as much as ten days is required for complete reaction. J. F. S.

A New Method for the Estimation of Electrolytic Conductivity of Solutions. JOHANNE CHRISTIANSEN (*Hospitalstidende*, **63**, 297—302; from *Chem. Zentr.*, 1920, iv, 568—569).—A

vessel with the liquid under investigation and a voltmeter are connected in series in a direct current circuit of known potential. If the resistance of the vessel is not negligibly small compared with that of the voltmeter, the latter does not indicate the known potential, but some lower value. A convenient vessel for the examination of urine is formed by a U-tube, the greater part of which is constructed from a capillary tube 32 cm. long and 1·8 mm. in diameter. The apparatus is calibrated with the aid of solutions of known conductivity. The method is useful when rapid estimations are required which need not be performed with extreme accuracy. H. W.

Electrical Conductivity of Gelatin Mixtures and their Behaviour during the Transition of the Gelatin. F. RETTIG (*Kolloid Zeitsch.*, 1920, **27**, 165—172).—The electrical conductivity of gelatin–water mixtures of concentrations 2·07% to 25·37% has been determined at 18°. The specific conductivity increases rapidly, and approaches at the higher concentrations to a maximum. Further measurements with gelatin–water mixtures to which additions of potassium chloride, bromide, or sulphate have been made in concentrations varying between 0·01*N* and 0·5*N*. The effect of the change of gelatin into β-gelatin has also been investigated by measuring the conductivity after the mixture has been heated at 80° for specified periods of time. When small quantities of salts are added to the gelatin–water mixture, the conductivity becomes greater than that of an aqueous solution of the added salt of the same concentration, but with a larger addition of electrolyte the results are reversed. If it be assumed that, on the addition of an electrolyte, the conductivity of the mixture is made up of the sum of the conductivities of the components, it follows that the conductivity calculated for the mixture is greater than the measured value, and increasingly greater the larger the amount of salt added. This reduction of the conductivity is attributed to the influence of the pure gelatin on the conductivity. The influence of gelatin on the conductivity of different salts may be expressed by a series similar to the Hofmeister series. On continued heating, the gelatin is gradually converted into β-gelatin. This change in the present case brings about an irreversible increased conductivity. The velocity of the change increases with the duration and temperature of the heating, and is greater in dilute mixtures than in concentrated mixtures. The addition of electrolytes effects the change in different ways, depending on the concentration and the nature of the ions of the electrolyte. J. F. S.

Electromotive Properties of certain Binary Alloys. I. Theoretical Considerations. ROBERT KREMANN (*Zeitsch. Metallkunde*, 1920, **12**, 185—191; from *Chem. Zentr.*, 1920, iii, 684).—A general theoretical account is given of the dependence of the potential of solid metallic alloys on their composition, and

the application of this relationship to the elucidation of their constitution. H. W.

Electromotive Properties of certain Binary Alloys. II. Electromotive Behaviour of Silver–Cadmium Alloys. ROBERT KREMANN and HELMUT RUDERER (*Zeitsch. Metallkunde*, 1920, **12**, 209—214; from *Chem. Zentr.*, 1920, iii, 684. Compare preceding abstract).—A series of cells composed of cadmium, cadmium sulphate, and cadmium silver alloys of varying composition have been examined, the initial potential observed immediately on bringing the electrodes into the solution, and the final potential, generally attained after six to eight hours, being observed. The initial potential sinks rapidly at first, then more slowly, and finally asymptotically approaches its final value. The initial potential of alloys richer in silver is somewhat variable. The less noble values only decrease slowly and fairly uniformly at first from the cadmium potential with increasing silver content (to about 50 millivolts), and only exhibit a marked drop in potential with more than 90 at. % silver; in addition to these less noble values, alloys containing more than 25% of silver exhibit higher initial potentials (as much as 150—170 millivolts greater than that of cadmium). Since this observation is also made with alloys which have been tempered at about 400°, the fluctuations cannot be attributed to failure to ensure equilibrium in their preparation. The initial and final potentials differ but little from one another with alloys containing up to 20 at. % of silver; from 20—40 at. %, the latter fall rapidly to the nobler potentials, and with increasing silver content approach the potential of pure silver asymptotically.

In the authors' opinion, the least noble of the measured initial values is the true potential of the alloy. The compounds present in the series of alloys, and also the mixed crystals up to about 90 at. % of silver are therefore but little more noble than cadmium. Owing to the absence of silver ions, it would be expected, on theoretical grounds, that silver would pass into solution and the potential gradually become less noble. The non-fulfilment of this expectation is explained by the authors on the supposition that local elements are immediately formed in which increasingly noble layers are developed by the solution of the less noble portions, and this hypothesis also accounts for the occurrence of more noble, as well as less noble, initial potentials. The falling away of the final potentials from 20 to 40 at. % of silver is probably to be ascribed to a galvanic resistance limit, such as has been described by Tammann. H. W.

Hydrogen Overvoltage. DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1920, **42**, 2233—2238).—The disagreement between the author and Newbery (A., 1920, ii, 727) depends, among other things, on difference in the use of the term "overvoltage." According to Newbery's implied definition, the expression should be reserved for potentials determined by a commutator device which periodically opens the exciting current at the electrode under

examination and closes the potentiometer circuit connecting this electrode and a reference electrode. In the work of MacInnes and Adler (A., 1919, ii, 131), and of practically every worker in this field, the exciting current remains flowing while the potentiometer measurements are made. Newbery appears to be nearly, if not quite, alone in thus restricting the meaning of the term. The difference between the two kinds of overvoltage is equal to Newbery's "transfer resistance."

The formation of a film of gas over the electrode, which Newbery considers as the source of transfer resistance, does not occur except over a very small part of the electrode used by the author, and the ohmic "transfer" resistance due to such a film is open to serious question.

Newbery's contention that transfer resistance may seriously affect conductivity measurements is not in agreement with the results of Eastman (A., 1920, ii, 578), which show that conductivities determined by direct and by symmetrical alternating-current measurements are equal within 0·02—0·03%, and also agree with Kohlrausch's values, although the latter were not determined with pure sine-wave current.

The "transfer resistance" of Newbery is probably a potential. It appears that all the facts, including those brought to light by Newbery's experiments, can be explained by the theory advanced by MacInnes and Adler. J. R. P.

Determination of the Hydrogen-ion Concentration in Pure Water by a Method for Measuring the Electromotive Force of Concentration Cells of High Internal Resistance. H. T. Beans and E. T. Oakes (*J. Amer. Chem. Soc.*, 1920, **42**, 2116—2131).—A new method of measuring the *E.M.F.* of concentration cells has been applied with an accuracy of 0·5 millivolt. The method consisted essentially in connecting the given cell with a standard condenser and discharging through a galvanometer. By comparing the deflexion with that given by a standard cell used under the same conditions, the ratio of the *E.M.F.* was found: $E_1/E_2=d_1/d_2$. The hydrion concentration of pure water is found to be $1{\cdot}23\times10^{-8}$, or $10^{-7{\cdot}91}$. The time required by the cell $Hg|HgCl,KCl|KCl|H_2O|H_2$ to charge a condenser of 1 microfarad capacity is three to five minutes. For a cell of low internal resistance, such as $Hg|HgCl,KCl|KCl|HCl|H_2$, only an instant is required to charge the condenser. The cell

$$Hg\,|\,HgCl,KCl\text{ sat.}\,|\,KCl\text{ sat.}\,|\,H_2O\,|\,H_2$$

reaches its maximum voltage in from forty minutes to one hour, and then remains constant for at least twenty-four hours.

J. R. P.

Electrolytic Pole-finder for Laboratory Use. Erwin Pinoff (*Chem. Zeit.*, 1920, **44**, 914—915).—For the detection of defects in electric leads and for the determination of polarity, the carbon filament lamp is replaced by two pieces of apparatus depending on electrolytic effects. In one, two burette clips are

fastened to a piece of glass, on which is laid a strip of paper moistened with water to which phenolphthalein has been added. Leads from the clips are applied to the circuit to be tested, and a red coloration under one clip indicates the cathode. In the other, the solution is contained in a short tube, from the ends of which the leads are taken. J. R. P.

Measurement of Electro-osmotic Tensions in Liquids of Low Conductivity. W. STASZEWSKI (*Krakau Anzeiger*, 1917, [*A*], 269—278; from *Chem. Zentr.*, 1920, iii, 782).—The term electro-osmosis is considered to denote the transport of a fluid along the surface of contact with a solid substance under the influence of an electric current; the converse phenomenon, the development of a current by the movement of two media along the surface of contact, is termed current stream. The movement of a liquid along the walls of the containing vessel when, for example, the fluid is positively charged relatively to the wall, causes a transport of electricity in the direction of the current. Under the influence of the external electric field, the charged liquid layer becomes set in motion, and carries with it the neighbouring particles in consequence of internal friction. If K is the DE, λ the specific conductivity, μ the coefficient of internal friction of the liquid, $(\phi_1-\phi_0)$ the difference of potential of the electrical double layer at the surface of contact of liquid and wall of tube, and P the difference of pressure at the ends of the capillary, the current developed by the flow of liquid in the capillary can be calculated from the formula $E=K(\phi_1-\phi_0)P/4\pi\lambda\mu$. In the present communication, which is devoted to the proof of this theory (as far as the dependence of electro-osmotic tension on external pressure is concerned) and to the estimation of the constants $K(\phi_1-\phi_0)$ of badly conducting substances, the author uses a method which depends on the measurement of the *E.M.F.* induced by driving a liquid through a capillary. The experiments were performed with nitrobenzene, ethyl ether, and mixtures of ethyl alcohol and toluene, and have shown that a proportionality exists between the electro-osmotic tension, B, and the external pressure, P. Further mixtures of alcohol and toluene show analogous variations with respect to λ and $K(\phi_1-\phi_0)$; both values decrease with the toluene content, slowly in mixtures poor in toluene, but rapidly in those rich in this substance, so that the ratio $K(\phi_1-\phi_0)/\lambda$ remains of the same order of magnitude, whilst λ diminishes in the ratio 1:10,000. There appears, therefore, to be an intimate relationship between the structure of the electrical double layer and the mechanism of electrical conductivity. Further measurements show that a marked increase in the conductivity of a badly conducting liquid raises the potential difference at the surface of contact with the solid substance. H. W.

A New Transport Apparatus. A. STEIGMANN (*Kolloid Zeitsch.*, 1920, **27**, 37—38).—The apparatus in use for the determination of the migration velocity of colloids has the disadvantage

that it may only be used for electrolyte-free, or at best electrolyte-poor, colloids. The Coehn-Galecki apparatus has been modified to overcome this difficulty. The U-tube is closed at the top by an horizontal tube, which connects both arms of the U-tube, and is itself connected to two small, vertical tubes in which the electrodes are placed. A long stop-cock passes through the middle of the cross-tube and into the bend of the U-tube. The stop-cock is bored so that when the horizontal cross-tube is open, the bend is closed by the stop-cock. The current is switched on with the U-tube open, that is, the current must pass through the colloid being measured; this takes place for a minute, during which time the electrolyte decomposition products remain in the electrode vessels. Then the stopper is turned to open the horizontal tube and, at the same time, close the U-tube, and, further, the direction of the current is changed. This flows through the horizontal tube, but cannot pass through the colloid under investigation, and reconverts the electrolyte decomposition products into the original electrolyte. After a minute, the tap and current are again changed, and so on. J. F. S.

Charging and Discharging Organic Dyes. ALBRECHT BETHE (*Kolloid Zeitsch.*, 1920, **27**, 11—17).—The velocity of kataphoresis of a number of acidic and basic dyes in acid and alkaline solutions of various concentrations has been examined with the object of ascertaining whether the charge on dye substance particles plays any part in the penetration of these substances into living cells. It is shown that all the sulpho-acid dyes migrate to the anode over a wide range of P_H values, but with different velocities varying with the P_H value. These substances, Chicago-blue, benzo-brown, and fast yellow, behave, as regards their coloured part, as true ions, since they are unchanged in the direction of their migration, but they differ from true ions, since the migration velocity does not remain constant with varying concentrations of hydrogen ions. Basic dyes also show a dependence on the hydrogen-ion concentration, but in the opposite sense to that of the acidic dyes. In this case, the smallest velocity is found in the neighbourhood of the neutral point, but generally slightly on the alkaline side of it. In the presence of larger quantities of sodium hydroxide, these dye substances partly change their direction; this is not due to the change in the P_H value, but to the formation of a sodium salt. J. F. S.

Determination of the Colloid Charge. RUDOLF KELLER (*Kolloid Zeitsch.*, 1920, **27**, 255—257).—An answer to the criticisms of Bethe (preceding abstract) concerning the results contained in a previous paper of the author (A., 1920, ii, 786). J. F. S.

Protein Reactions. I. A Microscopical Kataphoresis Method. A. VON SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1920, **110**, 116—118).—A microscopical kataphoresis device for application in colloidal chemistry is described. S. S. Z.

The Thermal Variation of the Coefficient of Magnetisation of some Anhydrous Chlorides and an Oxide in the Solid State, and the Theory of Magneton. PH. THÉODORIDÈS (*Compt. rend.*, 1920, **171**, 948—950).—The substances examined were cobalt, nickel and manganous chlorides, and manganous oxide. For the first two chlorides, the results obtained for the thermal variation of the coefficient of magnetisation agree with the theory of magneton. The values obtained for n, the number of magnetons, with manganous chloride or oxide are not whole numbers, but the differences between the atomic moments are very near to one magneton. All the chlorides give a positive constant of the molecular field. W. G.

Simple Electric Heater for the Evaporation of Liquids. EDUARD MOSER (*Zeitsch. angew. Chem.*, 1920, **33**, 300).—A mixture of coarse carbon powder and coarse fire-clay particles is placed in a shallow fire-clay vessel 20 cm. in diameter. Two iron electrodes are clamped inside the vessel and opposite each other, the lower ends of the electrodes making contact with the carbon mixture; the resistance of the latter is such that a current of 220 volts and 4 amperes yields a heat suitable for the evaporation of liquids. The resistance increases after the apparatus has been used for some time, but may be decreased by the addition of fresh carbon in small quantity. W. P. S.

The Isothermals of Hydrogen. L. HOLBORN (*Ann. Physik*, 1920, [iv], **63**, 674—680).—The isothermals of hydrogen at temperatures of 0°, 50°, and 100°, and at pressures between 20 and 100 atm., were determined. The results may be expressed in the following formulæ. The unit of pressure was that of a column of mercury of 1 metre at 0° under the normal gravity, $g=980{\cdot}665$ cm./sec.². The unit of volume was the volume of the gas under this normal pressure. Within the limits of experimental error, amounting to a few parts in ten thousand, the isotherms for 50° and 100° were linear; that for 0° showed a slight deviation from a straight line, but never to a greater extent than 1 in 1000.

$$0^\circ:\ pv=0{\cdot}99918+0{\cdot}00082094p+0{\cdot}0000003745p^2.$$
$$50^\circ:\ pv=1{\cdot}18212+0{\cdot}00089000p.$$
$$100^\circ:\ pv=1{\cdot}36506+0{\cdot}00091400p.$$

The results may be expressed as functions of $1/v$:

$$0^\circ:\ pv=0{\cdot}99918+(0{\cdot}00081613)/v+(0{\cdot}000001220)/v^2.$$
$$50^\circ:\ pv=1{\cdot}18112+(0{\cdot}0010505)/v+(0{\cdot}000001015)/v^2.$$
$$100^\circ:\ pv=1{\cdot}36506+(0{\cdot}0012450)/v+(0{\cdot}000001240)/v^2.$$

J. R. P.

Specific Heats. M. PADOA (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 198—202).—The author advances the view that the behaviour of solids with respect to specific heat should find its best interpretation in their chemical characters, these including the affinity. Application to this theme of the supposition, supported

by the author's experimental data (A., 1919, ii, 51, 96; 1920, ii, 85), that the binding of the atoms in crystals is due to chemical forces, and therefore to primary and secondary valencies, leads to the conclusion that the amplitude of the thermal movement of the atoms, and consequently also the heat-content and its derivative with respect to temperature, that is, the specific heat, should depend essentially on: (1) the solidity, (2) the directions, and (3) the number, of the linkings between the atoms.

Since the stability and the molecular complexity increase in passing from simple to complex molecules, it seems that a continually increasing affinity is rendered available for the construction of the crystalline edifice; confirmation of this is furnished by the fact that polymerides always melt at higher temperatures than the corresponding compounds with simple molecules. According to these considerations, both the solidity of the internal linkings of any single molecule and that of the external linkings uniting the various molecules of a chemical individual should tend to diminish the specific heat. That such diminution of the specific heat with polymerisation does actually occur is shown by the results of the author's measurements of the specific heats of cyanamide, dicyanamide, and melamine; silver cyanate and cyanurate; sodium cyanate and cyanurate; lævoglucosan, starch, and cellulose; cyanuric acid and cyamelide. For instance, the value of the specific heat for starch or cellulose is only about one-half of that for lævoglucosan. From the molecular heat, a mean atomic heat for each of the constituent atoms of a compound may be calculated, and this atomic heat, in contradiction of the law of Neumann and Kopp, decreases markedly as polymerisation increases. The different values of the specific heat for the isomeric cyanuric acid and cyamelide indicates, as was to be expected, that, other conditions being equal, the specific heat varies with the arrangement of the valencies in a molecule. T. H. P.

Specific Heat at Low Temperatures. PAUL GÜNTHER (*Ann. Physik*, 1920, [iv], **63**, 476—480).—The specific heat of sodium, antimony, and lithium hydride has been determined at various low temperatures by means of a slightly modified form of the Nernst and Schwers' apparatus (Günther, *ibid.*, 1916, **51**, 828). The following values have been obtained for the atomic heat in the case of the elements and the molecular heat in the case of lithium hydride: sodium, 87°, 5·26; 89·7°, 5·29; 91·5°, 5·40; 105·2°, 5·58; 108·0°, 5·64; 121·9°, 5·67; and 124°, 5·67; antimony, 80·4°, 5·19; 81·6°, 5·06; 85·6°, 5·22; 92°, 5·33; 98·1°, 5·47; lithium hydride, 74·0°, 0·674; 83·2°, 0·925; 90·5°, 1·217; and 292·7°, 8·177. The temperatures in all cases are in degrees absolute. The atomic heat and molecular heat values are compared with the values calculated by means of Debye's formula (A., 1912, ii, 1134), and in most cases a good agreement between the two sets of results is found. J. F. S.

The Theoretical Determination of the Vapour-pressure Equation for any Substance from the Density and Coefficient of Expansion at a given Temperature (below the Boiling Point). I. Carbon. J. J. VAN LAAR (*Rec. trav. chim.*, 1920, **39**, 647—655).—Applying the formula $\log p = -A/T - B\log T + CT + \ldots + C$ (compare A., 1920, ii, 287), the author obtains for carbon the equation $\log^{10} p = -47120/T - 3\log^{10} T + 20{\cdot}24$, from which he calculates for carbon $T_e = 5200°$ and $T_c = 7800°$ abs., and the value for the triple point of carbon as 3900° abs. The value of p_c is 2500 atm. (approx.). W. G.

A Method of Measuring Low Vapour Pressures, with its Application to the Case of 2:4:6-Trinitrotoluene. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1920, **42**, 2218—2221).—A McLeod gauge is immersed in a constant-temperature bath and connected with a bulb immersed in a second bath. The apparatus is exhausted, and nitrogen admitted to a small pressure. The pressure increase on heating the bulb is found. The material is placed in the bulb and the operation repeated, vapour being prevented from diffusing to the gauge by cooling a portion of the connecting tube. From the increase of pressure, the vapour pressure of the substance may be calculated.

The vapour pressures of trinitrotoluene, m. p. 80·5°, dried, but not specially purified, are represented in a table, from 80° to 102°, in the original. The observed pressures were: 0·046 mm. at 81·6°, 0·067 mm. at 90·1°, and 0·120 mm. at 102·6°. [See *J. Soc. Chem. Ind.*, 1921, 28A.] J. R. P.

Heat Changes in the Formation of "Nitrolime." PAUL DOLCH (*Zeitsch. Elektrochem.*, 1920, **26**, 455—459).—Making use of Nernst's heat theorem, the author has calculated the heat changes occurring in the formation of calcium cyanamide on the assumption of a complete equilibrium. The calculations are based on Thompson and Lombard's experimental data (*Met. Chem. Eng.*, 1910, **8**, 682). It is shown that the heat of combination of nitrogen with calcium carbide is $Q = 58700$ Cal. per gram of carbide. The equilibrium curve for the formation is deduced, and it is shown that the calculated values lie within the limits set by the uncertainty of the value of Q. The calculated values differ very much from the values of Thompson and Lombard at high temperatures, and it is suggested that the divergences may be due to a change in the phases of the system. J. F. S.

The Heat of Vaporisation of a Liquid at Low Temperatures. E. ARIÈS (*Compt. rend.*, 1920, **171**, 986—989. Compare A., 1920, ii, 585).—Polemical. A reply to Bruhat (A., 1920, ii, 732). W. G.

A Substitute for Thoulet's Solution. A. THIEL and L. STOLL (*Ber.*, 1920, **53**, [*B*], 2003).—For the determination of the specfiic

gravity of organic substances by Retger's suspension method, an aqueous solution of lead perchlorate can be used in place of the more expensive Thoulet's solution (mercury–potassium iodide) or Rohrbach's solution (mercury–barium iodide). The perchlorate solution is prepared by saturating commercial perchloric acid with lead carbonate and evaporating to the saturation point. The saturated solution at 15° is a mobile liquid, D^{15} 2·6, and contains 78% of lead perchlorate. E. H. R.

Forces in Surface Films. I. Theoretical Considerations. II. Experimental Observations and Calculations. III. The Charge on Colloids. A. M. WILLIAMS (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 223—234).—The effects of accessibility of surface and of adsorption on the apparent specific volumes of finely divided solids are discussed. Observations are in agreement with the theory of these effects. The true specific volume of a specimen of charcoal, which gave the apparent values 0·51 and 0·46 in water and chloroform, respectively, was evaluated as 0·67 c.c. per gram. The attractive pressure in the surface film on the charcoal was calculated to be of the order of 10,000 atm., whilst the internal pressure of charcoal itself was estimated as of the order of 50,000 atm. These compressive forces may give rise in the adsorption layer to a diffusion potential difference of the magnitude observed in the case of suspensoids. J. R. P.

Molecular Transformations in Thin Films on the Surface of Water. HENRI LABROUSTE (*Ann. Physique*, 1920, [ix], **14**, 164—238).—The effect of the following substances in forming films on the surface of water was studied: ethyl ether vapour, turpentine vapour, benzene, toluene, xylene, ethyl ether, light petroleum, turpentine, triolein, oleic acid, trilaurin, tribenzoin, salol, benzophenone, trimyristin, camphor, benzoic acid, lauric acid, vanillin, paraffin, palmitic acid, stearic acid, cetyl palmitate, cetyl alcohol, gamboge, cyclamine, and various powders. Betol, benzophenone, and azobenzene, added in solution, do not spread into films. The changes of certain films with time were investigated. J. R. P.

Theory of the Viscosity of Heterogeneous Systems. W. R. HESS (*Kolloid Zeitsch.*, 1920, **27**, 1—11).—After a discussion of the formulæ put forward by Einstein (*Ann. Physik*, 1906, [iv], **19**, 297) and Hatschek (A., 1911, ii, 19, 98) to represent the viscosity of heterogeneous systems, the author develops the formula $\eta_s = \eta(1 - K)$, in which η_s is the viscosity of the suspension, η that of the dispersion medium, and K the total volume of the suspended particles, that is, $(1 - K)$ is the volume of dispersion medium per unit volume of the suspension. Putting this formula into words, it states that the work used when a suspension flows through a tube of given dimensions is inversely proportional to the true cross-section of the liquid. The formula is tested by means of some experimental results on the viscosity of suspended blood corpuscles. It is found that the total volume

of the suspended particles must be multiplied by a factor slightly greater than unity to give the volume of the particles which is functioning in the process. The need of this factor is justified by the existence of a "dead space" in the liquid behind the solid particles, and this is taken account of in the formula by substituting $K' = aK$ in the original formula, where a is the factor mentioned above.

J. F. S.

Theory of the Viscosity of Heterogeneous Systems. A. EINSTEIN (*Kolloid Zeitsch.*, 1920, **27**, 137).—The author points out that he modified the formula for the viscosity of suspensions put forward in 1906 (*Diss.*, Berlin), which had the form $\eta' = \eta(1 + \phi)$, where ϕ is the total volume of the suspended particle in a liquid of viscosity η, to $\eta' = \eta(1 + 2 \cdot 5\phi)$ (*Ann. Physik*, 1911, **4**, 34). This change is apparently not well known (compare Hess, preceding abstract).

J. F. S.

The Importance of Adsorption in Analytical Chemistry. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1510—1529).—Although adsorption phenomena are comparable in many respects to those due to lowering of surface tension, the latter is not always the cause of the former, which generally proceeds in accordance with the law $x/m = ac . 1/n$, where x/m is the quantity of adsorbed material per gram of adsorbent, c is the end concentration, and a and $1/n$ are constants; this law may be regarded as in essence chemical, and based on the known laws of mass action.

In qualitative analysis, adsorption is of importance (1) for the collection of small quantities of material, as in the use of filter paper to collect lead in water analysis; (2) when traces of material may be lost by adsorption, generally on filter paper; and (3) for the removal of objectionable substances, as in the decolorising of liquids. In quantitative analysis, the same phenomena may appear. Adsorption of material, either by the filter paper or by a precipitate, may lead to grave errors in analysis. Thus filter paper strongly adsorbs various heavy metals from neutral solution. Quantitative determinations of the amounts so adsorbed show that lead is very strongly adsorbed, copper and silver to a smaller degree. After filtration of mercuric chloride, the ash-content of the filter paper, as determined by ignition, appears less, probably by volatilisation of the adsorbed mercury compound. According to Ostwald, it should be possible, by sufficiently numerous washings, almost completely to remove an adsorbed substance from filter paper, but this is not in agreement with the author's results.

The adsorbing action of filter paper, at least as far as electrolytes are concerned, is to be ascribed to the ash-content, which functions as a calcium-permutite, in which the calcium ion may be replaced by another positive ion, which thus becomes fixed in the paper. This view is supported by the fact that anions are not adsorbed, whilst if the solutions be sufficiently concentrated, equivalent quantities of positive ions are taken up, these quantities corresponding with the alkalinity of the ash. Acid solutions, that

is, hydrogen ions, prevent adsorption. By quantitative examination, it was found that metals of the alkalis and alkaline earths were not adsorbed, whilst the order for the quantities adsorbed from 100 c.c. of solutions of various common metallic salts containing 10 mg. per litre were as follows: $Pb^{\cdot\cdot}$ 90%, $Hg^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$ 80%, $Cu^{\cdot\cdot}$ 70%, $Cd^{\cdot\cdot}$ 60%, $Ni^{\cdot\cdot}$ 40%, $Co^{\cdot\cdot}$ and $Ag^{\cdot}$ 30%, $Zn^{\cdot\cdot}$ 10—20%, $Fe^{\cdot\cdot\cdot}$ nil. Alkaloids were also strongly adsorbed from neutral solutions. The capillary action of filter paper is obviously of great importance in this connexion, but the author does not accept the conclusion that this is explained by its adsorptive power. In some cases, the capillary working is purely physical, as in the case of white of egg and colloidal aluminium hydroxide, which act by blocking the pores. Positive colloids are difficult to filter; they give a precipitate in the pores of the paper, which is negatively charged. Filter paper will, in fact, impart a negative charge to positive metal oxide sols by repeated filtration.

The capillary action of filter paper in causing liquids to ascend is more complex. Ostwald's expression, $s=kt^m$, in which s is the height reached after the time t, and k and m are constants, m being less than unity, is found to hold for many cases. k is a characteristic constant, and corresponds with the speed of penetration for the paper. From the theoretical work of Lucas, the same result is deduced. Since the drawing up of dissolved substances is analogous to that of pure liquids, the former cannot be ascribed to adsorption. Schmidt has put forward the expression $h/H=k/K$, where h and H are the heights reached by the solute and the solvent respectively, and k and K are the constants in Ostwald's expression. From this law, when k and K are known, the concentration of a solution can be determined by the heights to which the solute and solvent, respectively, are drawn up.

Skraup and his pupils have studied these phenomena for acid solutions of different concentrations. Strong acids ascend less than water, weak acids nearly as high. Skraup arrived at the equation $(H-h)/h\,.\,c=K$, where H and h are the heights reached by the water and solute, respectively, and c is the concentration. The author finds the equation $L=aC^{1/n}$, where L is the ratio $h:H$, C is the concentration, and a and n constants, to hold for a large number of cases, notably hydrochloric, hydrobromic, and oxalic acids, and for the strong bases. The weak acids and bases are irregular, and no constants can be determined.

There are many abnormal cases; hydrogen fluoride and hydrogen sulphide behave as strong acids. By later work, Skraup has shown that the anion of the acid ascends as high as water, only the hydrogen ion being restrained; the author ascribes this to the alkalinity of the ash. Non-electrolytes suffer no restraint, and ascend as high as water. Salts behave as though highly hydrolysed. Salts of the alkalis and alkaline earths also ascend as high as water, but salts of the heavy metals are restrained. The rates of ascent vary considerably, and in some cases the solute is found to have higher concentrations the higher it ascends. The speed

of ascent is much diminished in presence of alcohol or glycerol, but the final height is not affected, except in the case of sodium hydroxide.

The author finds that whilst in neutral solution salts of the heavy metals are drawn up to a much smaller height than water, if the solutions be acidified, the salts reach to the same height as the water. This is regarded as further proof that the ascent is not a pure adsorption phenomenon. S. I. L.

Adsorption Compounds. III. R. HALLER (*Kolloid Zeitsch.*, 1920, **27**, 30—34. Compare A., 1918, ii, 259; 1919, ii, 184).—The adsorption complex produced when a suspension of lead hydroxide is shaken with cotton-red 4 B. extra,

$$C_{12}H_6Me_2(N_2 \cdot C_{10}H_5[NH_2] \cdot SO_3Na)_2,$$

has been treated with various reagents, some of which, acetic acid and sodium hydroxide, convert the lead hydroxide into a soluble compound, and others, hydrogen sulphide, hydrochloric acid, sulphuric acid, potassium chromate, and hydriodic acid, convert it into an insoluble compound. The object of the experiments was to ascertain in what way the adsorption complex is changed when the substrate is changed. The experiments show that the solution of the adsorbent completely destroys the complex. Chemical changes of the adsorbent, in the sense that a new, insoluble compound is produced, cause the destruction of the complex when the new product has no adsorptive action on the original dye, but when the new product exerts an adsorptive action on the dye, a new complex is formed without any apparent dissociation of the original complex. In the latter case there is an exception in the case of lead iodide. This substance does not adsorb cotton-red, but when the lead hydroxide is converted into lead iodide, a new complex is actually formed. J. F. S.

Relationship between Adsorption and the Dissolved Condition. I. Adsorption of Amino-acids, Polypeptides, and Egg-albumin by Animal Charcoal. EMIL ABDERHALDEN and A. FODOR (*Kolloid Zeitsch.*, 1920, **27**, 49—58).—Adsorption by charcoal from aqueous solution is theoretically considered, and it is shown that in the experiments on which the experimental law and the adsorption isotherm are based, dilute solutions were used with small quantities of the adsorbent, that is, although dilute aqueous solutions were employed, equilibrium was reached with concentrated charcoal solutions. It is therefore held that simple adsorption laws will only be obtained when the adsorbent is treated in the same way as the liquid solution. This is to be brought about by using a large amount of charcoal, so large that a further addition will not affect the partition of the dissolved substance between the liquid solvent and the solid adsorbent. From experiments on the adsorption of *l*-leucine and glycyl-*l*-leucine from aqueous solution (A., 1919, ii, 49, 50), it is shown that $x/(a-x)=k$ represents the process, in which a is the initial con-

centration, x the amount adsorbed, and k a constant. This relationship holds only when an excess of charcoal is used. From the above and other experimental results (*loc. cit.*), it is shown that the adsorption of amino-acids, polypeptides, and many other substances by charcoal occurs according to the partition law. The adsorption by charcoal is to be ascribed to chemical forces, since if this is not true, the adsorption of mixtures cannot be explained.

J. F. S.

A Capillary Phenomenon. H. BECHHOLD (*Kolloid Zeitsch.*, 1920, **27**, 229—233).—The author, in attempting to impregnate unglazed porcelain with an insoluble silver or copper salt, proceeded in the following way. The porcelain was placed in a vessel and the air removed by a pump, a solution of silver nitrate or copper sulphate was then admitted, and the porcelain saturated. This was then dried and again freed from air, and ammonium thiocyanate or sodium hydroxide, respectively, admitted; this was absorbed by the porcelain, and the insoluble salt formed. On drying and breaking the porcelain, it was found that the insoluble salts were not to be found in the interior of the mass, but were found entirely at the edges. On saturating porcelain, and, while still moist, breaking it, the absorbed salt was found to be uniformly distributed through the mass, so that the absorbed material travels to the edges on drying. The same phenomenon is found in agricultural earth which has been treated with mineral fertiliser; after long periods of drought, the mineral fertiliser is found in greater concentrations at the surface than elsewhere. Experiments are described on earth which had been uniformly mixed with 2% solutions of sodium chloride, barium chloride, and aluminium sulphate respectively, and kept for eleven months in a shaded place. On analysis, the salt concentration was found to have increased in the surface layers. Hypotheses to explain the phenomenon are put forward and discussed.

J. F. S.

Degree of Association of the Molecules of Binary Salts in Non-aqueous Solutions. P. WALDEN (*Kolloid Zeitsch.*, 1920, **27**, 97—101).—A general discussion of the association of the molecules of binary salts in non-aqueous solvents. Making use of previously published work on the conductivity and molecular weight of tetraethyl-, tetrapropyl-, and tetra*iso*amyl-ammonium iodides in a large number of solvents, it is shown that a connexion exists between the degree of association, x, and the dielectric constant, ϵ, of the solvent, in the sense that the degree of association increases with falling dielectric constant, and reaches its highest value with solvents of the smallest dielectric constant. Thus tetra*iso*amylammonium iodide in benzene solution (*DE* 2·3) and carbon tetrachloride solution (*DE* 2·2) behaves like a colloid and has a very large molecular weight, since it does not raise the boiling point of these solvents even when present in quantities up to 14%. Hence the conclusion is drawn that highly polymerised binary

electrolytes may pass through all conditions of molecular complexity, from simple ions to highly complex molecules typical of colloids, by dissolving them in suitable solvents. Solvents with dielectric constants >2 exercise a protecting action on highly polymerised molecules, and maintain the size at a point which is characteristic of colloids. Hence the author asserts that it is not so much a colloid type of material that has to be considered, but rather a colloidal condition of matter. J. F. S.

An Apparatus for Continuous Dialysis or Extraction. HUBERT MANN (*J. Biol. Chem.*, 1920, **44**, 207—209).—The apparatus consists essentially of a flask, a condenser, and a vessel so arranged that the system may be exhausted, and that the liquid placed in the apparatus may be caused to circulate by means of continuous evaporation and condensation. The apparatus has the advantages that a small amount of solvent can be used for the extraction of a large amount of material, and that the process may be carried out under reduced pressure. J. C. D.

Solubility. IV. Solubility Relations of Naphthalene and Iodine in the Various Solvents, including a Method for Evaluating Solubility Data. JOEL H. HILDEBRAND and CLARENCE A. JENKS (*J. Amer. Chem. Soc.*, 1920, **42**, 2180—2189. Compare A., 1916, ii, 578; 1918, ii, 36; 1919, ii, 392).—The solubilities of a substance in solvents where no molecular changes are involved, when plotted as $\log N$ (N = molar fraction) against $1/T$, give a family of approximately straight lines converging to the melting point of the solute, where $N=1$. The position of these lines corresponds with the internal pressures of the solvents, and is approximately predictable from them.

When solvation exists, the solubility will be greater than would otherwise be expected, but the temperature-coefficient will be smaller. The temperature-coefficient of solubility will be greatest for substances differing most in internal pressure.

The results are illustrated by the solubility of naphthalene and iodine in various solvents.

The solubilities of iodine in various solvents have been measured.

Solubilities of Iodine in Grams per 100 *Grams of Solution.*

	0°.	25°.	35°.	50°.
Heptane	0·6176	1·702	2·491	4·196
Carbon tetrachloride	0·6877	—	2·603	4·351

	25°.	30°.	35°.	40°.	45°.	50°.	56·64°.
Benzene	14·09	16·10	17·90	20·05	22·78	25·51	28·26

Violet solutions of iodine gave the family of curves expected, whereas the brown solutions showed the deviations expected for solvate formation. J. R. P.

Solubility. V. Critical Solution Temperatures of White Phosphorus with Various Liquids. JOEL H. HILDEBRAND and THEO. F. BUEHRER (*J. Amer. Chem. Soc.*, 1920, **42**, 2213—2218).—Critical temperatures of mixing of liquid phosphorus with other substances have been determined as follows: decane, >300°; chlorobenzene, 264°; naphthalene, 202°; phenanthrene, 200°; *p*-dibromobenzene, 163°; carbon disulphide, −6·5°. These figures confirm predictions made in previous papers (A., 1918, i, 62; 1919, ii, 392). J. R. P.

Crystallographical Observations on Atomic Structure. HERMANN TERTSCH (*Sitzungsber. Akad. Wiss. Wien*, I, **129**, pp. 24; from *Chem. Zentr.*, 1920, iii, 659—660).—The crystals even of the elements cannot, in general, be regarded as point lattices, since the individual components, the atoms, do not uniformly exhibit spherical symmetry, and also the symmetry of the components does not generally coincide with that of the lattice. The properties of Bohr's model do not indicate spherical symmetry of the atoms, although the discordance is not so marked if the path of the electrons is not regarded as lying in a plane. The crystalline forms of the several elements are compared with the object of elucidating regularities or detecting approximations in the individuals to spherical symmetry. The latter is found to be shown to a greater extent by the heavier than by the lighter elements. Special emphasis is laid on the possibility that the path of the electrons lies on the surface of a sphere, and the distribution of the electrons in such a system, and the type of symmetry which is thereby necessary for atomic structure, are discussed. The author further examines the possibility of coincidence between the hypothetical distribution of electrons thus derived (atomic symmetry) and the observed lattice symmetry. It is shown that a rational connexion exists between atomic symmetry and crystalline form. This is readily demonstrated for twenty-three of the forty-three crystallographically known elements; for four others, a suitable arrangement of electrons can be given provisionally, whilst for the remaining sixteen it is not at present possible to put forward a satisfactory hypothesis concerning the relationship of atomic and crystalline forms without resorting to very problematical suppositions. H. W.

Rôle of Water of Crystallisation and the Structure of Alums. L. VEGARD (*Ann. Physik*, 1920, [iv], **63**, 753—758).—Polemical with Schaefer and Schubert (A., 1919, ii, 516). Conclusions as to the situation of the atoms in space lattices cannot be drawn directly from the constitutional formulæ or from the indications of measurements of residual rays ("Reststrahlen"); the connexion between constitution, crystal structure, and the mechanism of residual rays must be established by determinations of the space lattice. It is incorrect to draw from the results of Schaefer and Schubert the conclusion that water of crystallisation enters into the

structure of the space lattice in the same manner as the other constituents of the salt. The opposite conclusion could equally well be drawn. J. R. P.

Relations between Crystallographic Phenomena and Constitution of some Organic Compounds. A. SCHLEICHER (*J. pr. Chem.*, 1920, [ii], **100**, 49—56).—A theoretical paper in which the relationship between constitution and crystalline form of organic compounds is discussed. J. K.

Limited "Free Rotation" from the Point of View of the Theory of Symmetry. A. SCHLEICHER (*J. pr. Chem.*, 1919, [ii], **100**, 57—64).—The ideas developed in the previous paper (preceding abstract) are applied to the cases of compounds, for example, *s*-dimethylsuccinic acid, which exist in two forms in consequence of suppression of free rotation. J. K.

The Structure of Precipitates. SVEN ODÉN (*Svensk Kem. Tidskr.*, 1920, **32**, 108—110; from *Chem. Zentr.*, 1920, iii, 705). —The increase in the size of the particles of barium sulphate is but little due to the difference in solubility of the small and large crystals. The change in the nature of the precipitate which is induced by heating depends on the fact that this is usually performed in a solution containing much free electrolyte, which catalyses the irreversible transformation of the secondary aggregates primarily formed. Reversibility appears to depend on the degree of hydration of the particles which are attached to one another by means of their aqueous envelopes. If for any reason the latter is broken or the original degree of hydration is too slight (as with metallic particles), so that the particles come within the range of their cohesive or adhesive forces, the transformation becomes irreversible. H. W.

The Velocity of Flocculation of the Selenium Sol. I. The Flocculation by Potassium Chloride. H. R. KRUYT and A. E. VAN ARKEL (*Rec. trav. chim.*, 1920, **39**, 656—671).—An extension of work already published (A., 1919, ii, 140). The variation of the number of particles with the time is, in principle, represented by Smoluchowski's formula (A., 1917, ii, 297), $\Sigma\nu=(\Sigma\nu)_0/(1+t/T)$, in the case of rapid flocculation, but in the case of slow flocculation this relation is not satisfied. Similarly, Smoluchowski's theory as to the relationship between the velocity of flocculation and the concentration of the sol holds good for rapid flocculation, but in the case of slow flocculation the phenomena are much more complicated. W. G.

The Coagulation of Gold Hydrosols by Electrolytes. The Change in Colour, Influence of Temperature, and Reproducibility of the Hydrosol. JÑANENDRA NATH MUKHERJEE and BASIL CONSTANTINE PAPACONSTANTINOU (T., 1920, **117**, 1563—1573).

Colloidal Adsorption. ARTHUR MUTSCHELLER (*J. Amer. Chem. Soc.*, 1920, **42**, 2142—2160).—With gelatin as a typical reversible colloid and zinc sulphate as electrolyte, the following results were found: (i) With small additions of electrolyte (less than 0·28 molar), the migration velocity of the anions was zero and that of the cations unity, so that the cations alone seem to carry the current; the anions alone are adsorbed, and only near the point where the colloid is neutral is there a small adsorption of cations; the colloid particles migrate to the negative pole, indicating that they are positively charged; the viscosity increases as the charge of the particles approaches the zero point; the rate of swelling of gelatin increases as the concentration of electrolyte approaches 0·28 molar.

(ii) When the concentration of electrolyte is 0·28 molar, the migration velocity of the anions is zero and that of the cations exactly unity. The electrolytic deposit on the cathode is smooth and pure. The anions and cations are adsorbed by the colloid in proportion to their mobilities; as the anions generally migrate faster than the cations, they are more adsorbed. The velocity of motion of the colloid particles in the electrostatic field is zero; the viscosity is a maximum; the rate of swelling of gelatin is a maximum.

(iii) With concentrations of electrolyte greater than 0·28 molar, the migration velocity of the anions is increased, and that of the cations is decreased, as the addition of electrolyte is increased. The adsorption of positive and negative ions continues until the particles assume a negative charge, when the cations are adsorbed in greater proportion. The particles migrate to the anode and are negatively charged, the viscosity of the solution gradually decreases as the charge on the particles increases; the rate of swelling of gelatin decreases as the concentration of electrolyte added increases. At molar concentration of zinc sulphate, gelatin is precipitated. J. R. P.

Investigation of Sodium Oleate Solutions in the Three Physical States of Curd, Gel, and Sol. MARY EVELYN LAING and JAMES WILLIAM MCBAIN (T., 1920, **117**, 1506—1528).

Colour Change of Congo-rubin with Time and the Influence of Electrolytes and Protecting Colloids. HEINRICH LÜERS (*Kolloid Zeitsch.*, 1920, **27**, 123—136).—The main factors which influence the colour change of Congo-rubin have been quantitatively studied. It is shown that the change is affected by the concentration of added electrolytes according to similar laws to those found for gold sols by Zsigmondy ("Kolloidchemie," 2nd edition, 353—354). A region of slow coagulation and one of rapid coagulation exist in which very small changes in the concentration of the electrolyte cause great changes in the time over which the colour change occurs. It is shown in the case of the three electrolytes, potassium chloride, magnesium chloride, and cerous chloride,

that the Whetham-Robertson coagulation rule is not followed. With a constant electrolyte concentration, the time of colour change of Congo-rubin is inversely proportional to its concentration. The time of change increases rapidly with the viscosity of the solution. Both these results are to be explained by the assumption that the coagulation of the discharged particles is controlled by their velocity of diffusion. The course of coagulation of a given sol under the influence of varying quantities of electrolytes is very similar within the limits of the present experiments. During coagulation an increase in viscosity takes place, which has not as yet been quantitatively explained. The protecting action of gelatin on the colour change of Congo-rubin is varying, depending on the concentration of the electrolyte. A minimum protecting action is obtained with moderate concentrations of electrolytes, but the action increases rapidly with larger or smaller concentrations. All internal changes of condition, such as are brought about by ageing, the influence of anions, and the action of tannic acid, have a very marked action on the protecting action of gelatin. This fact is evidence in support of the protecting sheath hypothesis of the protecting action, according to which the action is not due merely to the presence of the protecting colloid, but rather to close relationship between the protecting and protected colloids. The experiments all point to the fact that the change in the colour of Congo-rubin from red to blue under the influence of neutral salts, is a typical colloid-chemical phenomenon, and is very similar to the changes observed with gold sols. J. F. S.

Colloid Chemical Basis of the Kinetics of Fermentation. A. Fodor (*Kolloid Zeitsch.*, 1920, **27**, 242—249).—The author has derived expressions which represent the kinetics of ferment action. Two cases are considered, (i) where the ratio F/S is small, F is the free surface of the ferment, and S the concentration of the substrate, and (ii) where the ratio F/S is large. In the first case the velocity of reaction is given by $dx/dt = k(a-x)^{1/n}$, where a is the initial concentration of the substrate, x the amount changed in time t, n the constant of the adsorption isotherm $c_1/c_2{}^{1/n} = \text{const.}$, and k a constant. On integration the above equation gives $k = -n/(n-1)t\{\sqrt[n]{(a-x)^{n-1}} - \sqrt[n]{a^{n-1}}\}$. Inserting the value $n = \frac{1}{2}$, the equation becomes $k = 1/t(\sqrt{a} - \sqrt{(a-x)})$, and this equation has been found to represent the hydrolysis of glycyl-*l*-leucine by yeast extract in the presence of a hydrogen-ion concentration varying between $P_H = 6{\cdot}27$ and $8{\cdot}81$. In the second case, $dx/dt = k(A-x)^{1/n}$, where A is the concentration of the ferment and $1/n = 1$ or < 1. This, on integration, yields the formula $t = 1/(1-n)k\{A^{(1-n)} - [A-x]^{(1-n)}\}$. J. F. S.

"Gilding" of Amicrons of some Colloids. Gösta Börjeson (*Kolloid Zeitsch.*, 1920, **27**, 18—27).—The author has made use of the fact that solutions of gold amicrons can be used as crystallisation nuclei of other sols in the determination of the

degree of dispersity of sols with particles so small that they may not be counted in the ultramicroscope (Zsigmondy, A., 1906, ii, 679). The method consists in the preparation of a very highly disperse sol of the metal under investigation; a measured volume of this is added to a solution of gold chloride and hydrogen peroxide. The gold sol is formed on the amicrons of the highly disperse sol used, and from the rate of sedimentation the diameter of the gilded amicrons is deduced, and hence the number and radius of amicrons originally present. The formula $r_k = r\sqrt[3]{k/p}$ is used in the calculation, in which r_k is the radius of the amicron, r that of the sedimenting hydrosol, k the weight of the amicron, and p the total weight of the particles of the hydrosol. In this way the radius of the amicrons of alco-sols prepared by the Bredig method has been determined for the following metals: gold, $r = 4·9\ \mu\mu$; cadmium, $r = 9·9\ \mu\mu$; zinc, $r = 9·8\ \mu\mu$; silver, 7·1—18·0 $\mu\mu$, this value increasing with time; copper, $r = 5·0$—$7·8\ \mu\mu$. In the case of tin and bismuth, the particles can be seen in the ultramicroscope and their radii directly determined, the values obtained by the present method and the direct method are in fair agreement. Measurements have also been made with the sols of arsenic sulphide and antimony sulphide. J. F. S.

Colour Behaviour of Congo-rubin. R. Haller (*Kolloid Zeitsch.*, 1920, **27**, 188—195).—The colour changes of Congo-rubin have been studied. It is shown that Congo-rubin solutions change in colour from red to blue, by the addition of acid, sodium carbonate, barium hydroxide, and neutral salts, and the red colour may be recovered by the addition of alcohol. Further, a 1% solution of a bluish-violet colour on heating becomes red. If to 1 c.c. of the cold solution and to 1 c.c. of a warm solution 10 c.c. of water and 1 c.c. of magnesium sulphate solution (12·03 grams per litre) are added, the cold solution is immediately turned blue, whilst the warmed solution only becomes blue after some time. Loose strands of cotton, when coloured with a 1% solution of Congo-rubin by placing in the cold solution, slowly raising to the boiling point and then allowing to cool, take on a ruby-red colour of medium intensity. If the process is carried out in the presence of sodium chloride, the colour of the solution becomes blue, but on heating changes to red, and again the cotton is dyed red. On washing the cotton with distilled water it slowly changes to blue. If similar experiments are carried out with filter paper or cotton fabric, the colour is red, but except at the edges it does not change to blue on washing. This behaviour is explained by the presence of two phases of different dispersity in the solution; the one of greater dispersity is red and the other of smaller dispersity blue, and these are differently adsorbed by the cotton fibres. This is well seen with vicose silk, the red colour being visible through the blue. This view is confirmed by treating a 1% Congo-rubin solution with a large excess of sodium chloride and filtering; a red filtrate is obtained with a violet precipitate. The precipitate can be got into colloidal solution again in water, and is again treated with sodium

chloride and filtered, when again a red filtrate is obtained and a blue residue. On repeating this process five times a blue residue is finally obtained, which on washing gives a colourless filtrate. Consequently, the colloid has been separated into two parts of different dispersity. A number of experiments are made with Congo-rubin-*G*, which is found in many respects to be markedly different from Congo-rubin, although isomeric with it. The whole of the experiments point to the fact that the colour changes are colloid-chemical in character, and are due to the formation of a second phase of different dispersity from the original phase by the addition of electrolytes. J. F. S.

Apparatus for Ultra-filtration according to Gans. LEONOR SARLO VILLEGAS (*Contr. Estad. Ciencias [La Plata], Ser. mat. fis.*, 1919, **2**, 415—418; from *Chem. Zentr.*, 1920, iv, 613—614).—A simple, transportable apparatus for ultra-filtration is described, which is particularly suitable for colloidal solutions of metals. Solutions of silver, hæmoglobin, albumin, and milk, amongst others, have been investigated, and crystalloids which, for example, have been mixed with arsenic, have been separated quantitatively. The apparatus consists of a glass cylinder (9 cm. high and 7 cm. in diameter), provided with bronze disks as bases, which hermetically seal the cylinder by interspersed rubber rings. The upper disk has two openings, one for the manometer and the other for the pressure pump. At the bottom, between rubber ring and bronze disk, a thin, metallic plate is clamped which serves as support for the ultra-filter. Platinum is a suitable material for the plate, but nickel or aluminium can be used; it is provided with a number of holes, 1 mm. in diameter, to permit the passage of the filtrate. The following method is used in preparing the filter. Gun cotton (12·5 grams) is thoroughly moistened with alcohol, and as much ether is added as is required to bring the volume of the mixture to 500 c.c. A portion of this solution is brought on to a glass plate and dipped in water, when the mixture has set; a gentle movement of the plate causes the thin film to become detached. Filters of this type are permeable to colloids. In general, permeability depends greatly on the acidity, and is markedly increased by the presence of small amounts of acetic acid (about 0·5%). Collodion filters have also been investigated; variations of the solution have been examined, and very satisfactory results are recorded with mixtures of equal parts of alcohol and ether. The permeability of the collodion filters for colloids does not depend solely on the amount of acetic acid added, but also on the time which has elapsed since the addition was made. A collodion filter to which as much as 6% of acetic acid has been added gives a completely permeable filter if it is used immediately after being prepared. H. W.

Double Ternary Systems with Miscibility Gaps in the Liquid and Solid States. I. and II. C. MAZZETTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 150—153, 194—198).—I. The

author considers first the case of the double ternary system, in which only one binary system, corresponding with one side of the square, exhibits liquid and solid miscibility gaps with eutectics, the other three pairs forming continuous series of mixed crystals, and the surface ζ_l being below ζ_s. Diagrams of the system are shown. When two of the binary systems present solid and liquid miscibility gaps and eutectics, various cases occur: either these binary systems give rise to two pairs of gaps which have no mutual effect, in which event the condition of affairs is similar to that in which only one of the binary systems shows gaps; or the solid gaps alone, or else both solid and liquid gaps, fuse to a single gap.

II. Attention is given to a double ternary system in which three of the binary systems exhibit solid and liquid miscibility gaps and eutectics; in this case there appear in the system two compound gaps represented by two singular triangles, one of three liquids and one of three solids. The case of four miscibility gaps in the system is also considered. T. H. P.

Equilibria of Reciprocal Salt Pairs, Sodium Chloride, Magnesium Sulphate and Sodium Sulphate, Magnesium Chloride at 25°. SHIRŌ TAKEGAMI (*J. Tokyo Chem. Soc.*, 1920, **41**, 831—868. Compare Blasdale, A., 1920, ii, 237).—Solubilities of the four salts and the equilibrium of two salts having a common ion were investigated; that of magnesium chloride and sulphate was especially studied, ascertaining the formation of four hydrates of magnesium sulphate, proposed by van't Hoff. In the equilibria of reciprocal salt pairs, nine solid phases exist: Na_2SO_4; $Na_2SO_4,10H_2O$; NaCl; astracanite; $MgSO_4,7H_2O$; $MgSO_4,6H_2O$; $MgSO_4,5H_2O$; $MgSO_4,4H_2O$; and $MgCl_2,6H_2O$. Compositions of the solution saturated with one, two, or three salts were as follows, where *a*, *b*, and *m* are expressed by the formula:

$$100mH_2O,aNa_2(100-a)Mg,bCl_2(100-b)SO_4.$$

Solid phase.	*a*.	*b*.	*m*.
NaCl	100	100	18·02
$MgSO_4,7H_2O$	0	0	18·31
$Na_2SO_4,10H_2O$	100	0	28·51
$MgCl_2,6H_2O$	0	100	9·41
NaCl; Na_2SO_4	100	80·40	15·96
Na_2SO_4; $Na_2SO_4,10H_2O$	100	51·31	18·03
NaCl; $MgCl_2,6H_2O$	1·08	100	9·32
$MgSO_4,7H_2O$; astracanite	32·72	0	13·69
Astracanite; $Na_2SO_4,10H_2O$	50·14	0	13·97
$MgSO_4,7H_2O$; $MgSO_4,6H_2O$	0	86·81	12·08
$MgSO_4,6H_2O$; $MgSO_4,5H_2O$	0	91·10	10·15
$MgSO_4,5H_2O$; $MgSO_4,4H_2O$	0	93·60	9·56
$MgSO_4,4H_2O$; $MgCl_2,6H_2O$	0	93·58	9·11
$Na_2SO_4,10H_2O$; Na_2SO_4; astracanite	57·95	13·88	13·66
Na_2SO_4; NaCl; astracanite	73·38	70·66	15·06
NaCl; astracanite; $MgSO_4,7H_2O$	37·97	49·71	13·96
NaCl; $MgSO_4,7H_2O$; $MgSO_4,6H_2O$	3·77	87·04	11·92
NaCl; $MgSO_4,6H_2O$; $MgSO_4,5H_2O$	0·68	91·12	10·03
NaCl; $MgSO_4,5H_2O$; $MgSO_4,4H_2O$	0·25	93·7	9·5
NaCl; $MgSO_4,4H_2O$; $MgCl_2,6H_2O$	0·24	93·77	9·27

K. K.

The Determination of the Number of Independent Constituents. Dubreuil's Rule; the Action of Water on a Mixture of Salts. C. RAVEAU (*Compt. rend.*, 1920, **171**, 913—916).—Dubreuil's rule (A., 1920, ii, 742) is discussed, and Rengade's work (A., 1917, ii, 451) on the purification of salts by fractional crystallisation is discussed in the light of this rule.

W. G.

The Separation of Two Salts having a Common Ion. A. TH. SCHLŒSING (*Compt. rend.*, 1920, **171**, 977—981).—Curves are plotted showing the weight of each salt in 1 kilo. of solution saturated with respect to the two salts at different temperatures. The solution containing the two salts, which it is required to separate, is analysed, and from these results and the curves previously plotted it is possible to determine the temperature at which the solution should be evaporated, so that only one salt will separate out. W. G.

Periodic Precipitation and Coagulation by Electrolytes. FRANZ SEKERA (*Kolloid Zeitsch.*, 1920, **27**, 28—30).—A theoretical paper, in which the author considers the causes of periodic precipitation and coagulation of colloidal solutions in layers by means of electrolytes. J. F. S.

The Phase Rule. HENRY LE CHATELIER (*Compt. rend.*, 1920, **171**, 1033—1038).—A critical survey of Gibbs' phase rule and of the criticisms of it which have appeared in recent years. The criticisms urged against it are briefly replied to. W. G.

Radiation as a Factor in Chemical Action. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1920, **42**, 2190—2205).—In order to explain the close similarity between the Arrhenius equation for the velocity of chemical reactions and the Wien radiation law (namely, that the logarithms of the reaction velocity and of the intensity of monochromatic radiation are both linear functions of the reciprocals of the absolute temperature), and also to explain the fact that the velocity of a unimolecular reaction is independent of the collision frequency of the molecules, it has been assumed that molecules can take part in chemical reactions only after they have become activated, and that the activation is brought about by the absorption of nearly monochromatic radiation. There seems to be ample evidence in support of the activation of molecules, but the radiation hypothesis does not seem to rest on such a firm foundation.

There are two decisive tests of the validity of the radiation hypothesis: (1) the reacting substance must absorb radiation of the frequency required to produce activation, and there must therefore be an absorption band which includes this frequency; (2) the total amount of radiant energy absorbed must be sufficient to supply the heat of activation of the molecules, which is calculated from the temperature-coefficient of the reaction velocity.

Examination of the available data indicates that there is little evidence that absorption bands occur which include the frequency corresponding with the activation. In the dissociation of phosphine, nitrous oxide, nitric oxide, carbonyl chloride, phosphorus and arsenic, the activation frequencies lie within the range of the visible spectrum, although the gases are all colourless.

The data for phosphine show that the energy required for activation of 1 c.c. at 948° abs. is 4×10^{10} times greater than the amount which could be supplied by radiation from 1 sq. cm. of surface at this temperature. Also, when the intensity of the radiation is increased enormously (as by using daylight), the reaction velocity does not show a corresponding increase.

Experiments with nitrogen peroxide, hydrogen, and iodine vapour show that the heat conductivity of dissociating gases is many times greater than that of similar gases which do not dissociate. The increase in heat loss from small wires, due to the dissociation of the surrounding gas, is often more than ten times the total energy radiated from the wire. On the basis of the radiation hypothesis, however, the dissociation entails an absorption of radiation, and could produce only a decrease in heat loss from the wire. These experiments furnish conclusive evidence against the radiation hypothesis.

The similarity between the Arrhenius and Wien equations results from the fact that both reaction velocity and radiation are fundamentally dependent on phenomena involving probability. Both equations can be deduced from the same statistical law: $P=ce^{-E/kT}$, where P is the probability that, in any large number of molecules in thermal equilibrium at the temperature T, a given molecule shall have an energy lying between E and $E+dE$. It is shown that, unless the law of conservation of energy has also only a statistical significance, the activation energy must be derived from internal energy of the molecules, which exists at the zero of absolute temperature. The very fundamental difficulties involved in this conclusion are of the same nature as those encountered in the theory of the photoelectric effect, thermionic emission, and other phenomena involving quantum relations. J. R. P.

The Laws Governing the Propagation of Combustions. L. Crussard (*Technique moderne*, 1920, **12**, 243—250, 295—301).—This is a mathematical discussion of gaseous combustions, from the standpoint of Hugoniot's law, covering detonations and deflagrations; stability of propagations including propagation of simple mechanical perturbations, velocities of combustions, and of sound, rôle of calorific exchanges, flame and preflame, intrinsic stability, examination of the different systems of combustion from the point of view of intrinsic stability, extrinsic stability and instability, encounter of the flame and mechanical shock, detonations from the point of view of extrinsic stability, compressions and deflagrations; the explosion wave; propagations in their relations to the liveliness of combustions, examination of the essential data including reaction

velocity, temperature of inflammation and diagrams of combustion; the law governing deflagration including the study of the preflame and the flame; the law of combustion, the order of the velocity of propagation in the usual mixtures, velocity of propagation in the most rapid mixtures, rôle of the temperature of origin, limits of aptitude for the propagation of deflagration and tests of the general formula for the velocity of propagation; and finally a discussion of the constitution of flame. CHEMICAL ABSTRACTS.

Behaviour of Explosive Mixtures of Gases at Low Pressures. A. STAVENHAGEN and E. SCHUCHARD (*Zeitsch. angew. Chem.*, 1920, **33**, 286—287).—Mixtures of methane and air were sparked in a U-tube of 250 c.c. capacity, with limbs about 2·5 m. long and 12 mm. in diameter. The level of mercury in the apparatus afforded a measure of the pressure to which the gas was subjected. The results showed that explosive mixtures of gases have a critical pressure below which they no longer ignite. The intensity of an explosion decreases with the fall in the pressure. By carrying out the experiment in the dark it is possible to determine from the character of the flash whether the explosion is complete, or whether there has only been partial combination. For example, 5 c.c. of the gas under a pressure of 40 mm. of mercury showed a flash of about 30 mm. in length, and 6% of the gas combined, whilst 9·5 c.c. of the gas under a pressure of 61 mm. of mercury showed a flash 150 mm. long and 30% of the gas combined. A slow, flameless combination takes place at pressures below the critical point, the amount of such combination increasing with the nearness of the pressure to that point. The critical pressure depends on the nature and proportions of the gaseous constituents, the moisture, and the initial impulse. The occurrence of an explosion in a closed space does not prevent the possibility of a second explosion, without any subsequent change having been made in the proportions of the mixture. The lower the pressure at the first explosion, or the greater the reduction in the pressure by that explosion, the greater will be the possibility of a second explosion (compare Mason and Wheeler, T., 1918, **113**, 45). C. A. M.

Velocity of Decomposition of High Explosives in a Vacuum. II. Trinitrophenylmethylnitroamine (Tetryl). ROBERT CROSBIE FARMER (T., 1920, **117**, 1603—1614).

The Transformation of Ammonia into Carbamide. C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1920, **171**, 1003—1005).—The authors obtain the expression

$$\log p = -1511/T + 5{\cdot}6 \log T - 9{\cdot}4,$$

where p is expressed in atmospheres, for the value of the equilibrium pressure of ammonium carbamate at different temperatures in an enclosed space, such that the volume occupied by the gaseous phase is as small as possible. W. G.

The Velocity of the Diazotisation Reaction as a Contribution to the Problem of Substitution in the Benzene Nucleus. J. Böeseken, W. F. Brandsma, and H. A. J. Schoutissen (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 249—266).—The influence of substituents in the nucleus on the rate of diazotisation of aromatic amines was studied in connexion with the general problem of substitution in the benzene ring. The diazotisations were carried out at 0° in solutions containing two millimols. of amine per litre. At convenient intervals, samples of the solution were removed and coupled in alkaline solution with Schäffer's salt at 0°, and the extent to which diazotisation had proceeded was estimated by a colorimetric comparison of the samples, assuming that diazotisation was complete in six hours. In each case the reaction was bimolecular, and the velocity constants found were as follows: aniline, $100K = 0{\cdot}0965$; *o*-toluidine, 0·0928; *m*-toluidine, 0·137; *p*-toluidine, 0·0687; *m*-xylidine, 0·0886; *o*-chloroaniline, 0·483; *o*-bromoaniline, 0·450; *o*-iodoaniline, 0·453; *m*-chloroaniline, 0·135; *m*-bromoaniline, 0·142; *m*-iodoaniline, 0·1515; *p*-chloroaniline, 0·153; *p*-bromoaniline, 0·129; *p*-iodoaniline, 0·1505; aniline-*o*-sulphonic acid, 0·966; aniline-*m*-sulphonic acid, 0·107; aniline-*p*-sulphonic acid, 0·247; anthranilic acid, 1·761; *m*-aminobenzoic acid, 0·145; *p*-aminobenzoic acid, 0·521; and *m*-nitroaniline, 1·13. Except in the toluidines and xylidine, the velocity of the reaction is considerably increased by introducing substituents into aniline. The effect is greatest when the substituent is in the ortho-position to the amino-group, and weakest in the meta-position. The velocity increases with the negative character of the substituent. E. H. R.

Alkaline Hydrolysis of Esters of Symmetrical Homologues of Oxalic Acid. Anton Skrabal and Erna Singer (*Monatsh.*, 1920, **41**, 339—400).—The authors have investigated the hydrolysis of esters of symmetrical homologues of oxalic acid in aqueous and aqueous-alcoholic solution by means of sodium carbonate and hydroxide, and have measured the velocities of the two stages of the reactions.

In concentrated solution, the esters of the normal acids from oxalic to sebacic acid exhibit normal behaviour, the reaction being a simple stage reaction of the second order. The ratio between the reaction constants of the two consecutive reactions has its maximum value for oxalic acid, afterwards falls rapidly, and then slowly approaches the limiting value, 2, for the higher homologues. Further, this ratio is not independent of the concentration, but for one and the same dicarboxylic acid diminishes apparently to the same limit, 2, as the concentration is increased. This limit is far from attained with the lower homologues, but is practically reached with such esters as those of azelaic and sebacic acids. These results are similar to those obtained by Chandler (A., 1908, ii, 467), who found that the ratio between the two electrolytic dissociation constants of the free dicarboxylic acids approaches the limiting

value, 4, as the molecular weight of the acids and the concentration increase. The two ratios are, indeed, symbatic, and reach their limiting values simultaneously, and the two limiting values correspond with the independent, uninfluenced reaction of the two identical reactive groups.

The ratio 2 as the limit for the kinetic constants, and the approximation to this limit as the concentration and velocity increase, are easily interpreted according to the "regulation" law (A., 1912, ii, 33; 1916, ii, 606), which states: If alteration of a parameter of the velocity of reaction (such as the nature or concentration of the reacting substances, the medium, the nature and concentration of the catalyst, the temperature, or the illumination) produces increase of this velocity, influences come into play in the form of alteration of the constants, or of the form of the time-law, which are antagonistic to such increase; thus the actual regulated velocity lags behind that which would be expected in absence of regulation. The ratio between the constants is the ratio of two comparable velocities. If the latter are subject to regulation, as the velocity increases, the more rapid reaction is relatively more highly retarded than the slower one, the ratio approaching the value 2; when the latter is reached, the two groups react equally quickly, and beyond that stage both velocities are retarded to the same extent, and the ratio hence undergoes no further change.

From alterability of the constant-ratio follows, necessarily, that of the velocity-coefficients. On hydrolysis of ethyl malonate and succinate in dilute solution, a decline of the constants of the second order is, indeed, observed.

Whilst increase of the coefficients is observed, or, more accurately, suggested, in the case of the normal acids only in dilute solution, the diminution in the coefficients with esters of the alkylmalonic acids is so considerable that the reaction cannot be calculated as of the second order. This diminution is greater in dilute than in concentrated solution, and greater with the dialkylmalonic esters, which are hydrolysed slowly, than with those of the monoalkylmalonic acids, which are hydrolysed more rapidly, and still greater than with the malonic esters, which undergo hydrolysis with great rapidity. T. H. P.

Influence of Lead on the Catalytic Activity of Platinum. EDWARD BRADFORD MAXTED (T., 1920, **117**, 1501—1506).

Catalytic Studies. VII. Catalysis of Hydrogen Peroxide by Iodine Ions. E. ABEL (*Monatsh.*, 1920, **41**, 405—421).—The author has already shown (A., 1908, ii, 939) that the catalysis of hydrogen peroxide by hydrogen ions, often cited as a typical catalysis (Bredig and Walton, A., 1903, ii, 282), may be represented as a special case of a much more general catalysis of the peroxide which results from the co-operation, or, more accurately, the antagonism, of the two reactions: (1) $H_2O_2 + I_2 \longrightarrow 2H^{\cdot} + 2I' + O_2$, and (2) $H_2O_2 + 2H^{\cdot} + 2I' \longrightarrow I_2 + 2H_2O$. The kinetics of the second of these reactions has been long worked out

(Noyes and Scott, A., 1896, ii, 158; Brode, A., 1901, ii, 443; 1904, ii, 718), and the author has recently (*Zeitsch. physikal. Chem.*, 1920, **95**, 513) investigated the kinetics of reaction (1).

The conditions for the initiation of the catalysis of hydrogen peroxide by iodine ions are now formulated, and the result arrived at tested by means of the experimental material formerly obtained (*loc. cit.*). For a given case of this catalysis, the position of the spontaneous catalytic equilibrium and the time relations leading to its attainment are calculated and discussed. T. H. P.

The Temperature-coefficient of the Decomposition of Hydrogen Peroxide by Fat Catalase. E. NORDEFELDT (*Biochem. Zeitsch.*, 1920, **109**, 236—240).—The constant A of Arrhenius's formula has been determined for the decomposition of hydrogen peroxide by fat catalase at various temperatures. The figures obtained did not differ much from those obtained by Senter for blood catalase. S. S. Z.

Catalysis. VIII. NIL RATAN DHAR [with A. K. DATTA and D. N. BHATTACHARYA] (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 299—307).—The paper deals with the effect of catalysts on the reaction between ferrous ammonium sulphate and silver nitrate and on the atmospheric oxidation of sodium sulphite solutions, and with the hydrolysis of methyl acetate by oxalic and picric acids in presence of potassium oxalate and sodium picrate, respectively. The reaction between ferrous ammonium sulphate and silver nitrate is bimolecular and very rapid at 0°, with a small temperature-coefficient. After a time, an equilibrium is set up, due to the reducing action of silver on ferric nitrate:

$$Ag + Fe(NO_3)_3 \rightleftharpoons AgNO_3 + Fe(NO_3)_2.$$

The reaction is accelerated by acids, including nitric, sulphuric, citric, tartaric, acetic, and carbonic, but not by boric acid or phenol. Manganese salts and potassium nitrate have a retarding effect.

A large number of organic substances act as negative catalysts with respect to the atmospheric oxidation of sodium sulphite. Organic acids have practically the same effect as their sodium salts, and benzoic, oxalic, and salicylic acids have a greater negative effect than the weaker organic acids. Quinol was the most powerful negative catalyst discovered. The temperature-coefficient of the reaction, which is 2 between 25° and 40°, was not affected by the negative catalysts. Organic substances probably act as negative catalysts by diminishing the concentration of the sulphite ions, with which they combine to form stable complexes.

Potassium oxalate in increasing concentration steadily diminishes the velocity-coefficient of hydrolysis of methyl acetate by oxalic acid, whilst in the case of picric acid the velocity constant first increases to a maximum value and then falls off with increasing concentration of sodium picrate. These results may be explained by considering, besides the diminution of hydrogen-ion concentration due to the increased concentration of the negative ion common

to the acid and salt, the increased dielectric constant and ionising power of the solvent caused by the dissolved salt. E. H. R.

Catalysis. IX. Thermal and Photochemical Reactions. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 308—312).—It is shown that many reactions having large temperature-coefficients are sensitive to light, and hence it is considered that sensitiveness to temperature and to light influences have a common cause. The reaction between iodine and potassium oxalate is accelerated by light, the most active portion of the spectrum being the indigo near the violet end. Mercuric chloride and potassium oxalate in sunlight undergo the reaction:

$$2HgCl_2 + K_2C_2O_4 = 2KCl + 2CO_2 + 2HgCl.$$

This reaction is also induced by the light from a carbon arc, a quartz mercury vapour lamp, or an arc between electrodes of thoria and zirconia. Ammonium cupric oxalate is decomposed by tropical sunlight, but not by the above artificial sources of light. Uranium salts are general positive catalysts in photochemical reactions, whilst manganese salts are general negative catalysts in both light and dark reactions. The author's conclusions on the relation between thermal and light effects are supported by Perrin's hypothesis that all chemical reactions are induced by radiations (A., 1919, ii, 177). E. H. R.

Catalysis. X. Explanation of some Abnormally Large and Small Temperature-coefficients. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 313—318).—The reaction between iodic acid and potassium iodide in dilute solution is very rapid at 0°, and the temperature-coefficient cannot be determined, but is practically equal to unity. In presence of sodium and magnesium sulphates, slightly less iodine is liberated at higher than at lower temperatures, and the temperature-coefficient appears to be negative. This is due to hydrolysis of the sulphate at higher temperatures, with formation of OH' ions, which react with the iodine liberated. In presence of ammonium and zinc sulphates, the reaction apparently has a positive temperature-coefficient, the explanation being that at higher temperatures these salts produce $H^{\cdot}$ ions, which are active in liberating iodine. The abnormally large temperature-coefficient of the reaction $3I_2 + 6OH' = 5I' + IO_3' + 3H_2O$ in presence of sodium carbonate and hydrogen carbonate is due to hydrolysis of the carbonates. A number of other temperature-coefficients are similarly explained.
E. H. R.

A New World of Chemical Compounds. P. P. VON VEIMARN (*Ann. ecole mines de l'Oural*, 1919, **1**, 1—7).—The assertion that atomic and molecular forces are vectorial is identical with the principle that chemical forces have a vectorial character. Hence a change from gas–fluid to solid–crystal is a chemical process. Chemically homogeneous crystals are the simplest representatives of homochemical compounds, that is, compounds in which affinity

reveals itself between similar atoms, and all liquids and gases must be considered as disperse systems of this vectorial polymer-crystal. If such crystals are chemical compounds, it follows, of necessity, that the valency of atoms of all elements cannot be less than 6 in order to give a three-dimensional form. Differences in combining power with hydrogen or oxygen atoms lie largely in the size of the surface of atoms and in the ease with which hydrogen atoms in their mobility may form doublets, thus hindering the concentration of hydrogen atoms round the atom of the element. Molecules of hydrogen, fluorine, nitrogen, etc., are examples of the most stable homochemical compounds, and show by the tendency to remain as doubled atoms the magnitude of the intensity of homochemical forces. In chemical compounds the atoms have not lost, but only more or less changed, the properties they have in the free state. A study of colloidal synthesis has given rise to the principle that any matter gives in corresponding conditions homochemical compounds with any other matter, in case of there being common atoms or atomic groups. Dispersoidal parasitism with homochemical compounds thus has rendered possible the preparation of colloidal solutions of great stability and high concentration.

CHEMICAL ABSTRACTS.

Arrangement of Atoms in some Common Metals. A. W. HULL (*Science*, 1920, **52**, 227—229).—A preliminary note on the results of *X*-ray analysis of various metals. Calcium has a face-centred cubic arrangement, each atom being surrounded by 12 equi-distant atoms. Titanium is centred cubic, each atom being surrounded by 8 others. Zinc is hexagonal close-packed and elongated 14% in the direction of the hexagonal axis. Cadmium is like zinc, with an elongation of 16%. Atoms of indium are arranged in a face-centred tetragonal lattice resembling a cubic close packing, except that it is elongated 6% in the direction of one of the cubic axes. Ruthenium has an arrangement similar to zinc and cadmium, but there is a contraction of 3% in the direction of the hexagonal axis. Palladium, iridium, and platinum are like calcium; tantalum is like tungsten, iron, chromium, and titanium.

CHEMICAL ABSTRACTS.

A Convenient Form of the Periodic Classification of the Elements. C. R. NODDER (*Chem. News*, 1920, **121**, 269).—A modification of Harkin's spiral as a representation in one plane. Two plane spirals are used, for the odd and even series, respectively, corresponding radii being parallel and numbered similarly.

J. R. P.

Nature of Valency. ALFRED BENRATH (*Zeitsch. angew. Chem.*, 1920, **33**, 289—290).—The following conception of valency is suggested to reconcile the theory of Berzelius with observed facts. The reactions attributable to the main valencies of an element are characterised by the combination of atoms with other atoms of opposite polarity, and their replacement by other atoms with similar

action, whereas by-valencies are characterised, in the main, by the combination of compounds, and rarely by the combination of atoms of similar polarity. Hence by the valency of an element should be understood only the number of main valencies not altered by the action of by-valencies. The main valencies must be either positive or negative, and if an element appears to exert valencies of opposite polarity, the explanation is to be found in the presence of by-valencies. The valency towards hydrogen, or (+) valency, is distinguished from the valency towards oxidising agents, or (−) valency, and these cannot be simultaneously active in the same element, since hydrogen combines with oxidising elements to form inactive compounds, such as water or hydrogen chloride, which can only enter into combination with by-valencies. The valency of an element in a compound can only be changed by oxidation or reduction, and not by reactions involving the by-valencies. C. A. M.

Angle of Slope. A New Physical Constant. A. LANGHANS (*Kolloid Zeitsch.*, 1920, **27**, 101—123).—The angle of slope is that angle at which a particle of material can just maintain its position. The author describes six methods by which this angle may be measured. One of these consists in filling a metal cylinder, which is cut into two pieces, with the powdered substance, then, on removing the metal cylinder, the powder will fall and produce a cone, which may be measured. The angle which the side of the cone makes with the horizontal is the angle of slope. This angle has been determined for ninety substances; the results are given in tables, together with the specific gravity and the size of the particles. The angle is shown to decrease with increasing specific gravity, and it also depends on the viscosity of the powder and the size of the particles. J. F. S.

The Accuracy obtainable with Varnished Weights. E. H. VOGELENZANG (*Chem. Weekblad*, 1920, **17**, 453).—Aluminium weights varnished over to varying thicknesses have been exposed to atmospheres saturated to various known degrees of moisture, and the alteration in weight examined. It is found that no perceptible change occurs, and such weights are thought to be suitable for use even with the microbalance, since the humidity of the air in the case can be kept almost constant. S. I. L.

The Metallic Elements of the Ancient Chinese. G. WANG (*Science* [China], 1920, **5**, 555—564).—The Chinese early discovered a number of chemical facts and a knowledge of the chemical character of some natural phenomena. The discoveries were never scientifically developed, and the surviving accounts are mystical and obscure. The author gives an account of the metallurgy of early China. CHEMICAL ABSTRACTS.

The Metallic Compounds of the Ancient Chinese. G. WANG (*Science* [China], 1920, **5**, 672—684).—The author divides the history of chemistry in China into: (1) the alchemical period; (2) the period of iatro-chemistry; (3) the modern period. China has just emerged from the second period. A large number

of the common inorganic compounds were known and employed as medicines. Investigation has been made of the reactions involved in the old methods of preparing these compounds.

CHEMICAL ABSTRACTS.

Inorganic Chemistry.

Influence of Chloride on the Solubility of Chlorate and its Dependence on Temperature. JEAN BILLITER (*Monatsh.*, 1920, **41**, 287—295).—In spite of the very considerable increase in the solubility of chlorates with rise of temperature, but little separation of crystals occurs when a hot solution, saturated with chlorate and very rich in chloride, is cooled. Investigation shows that the solubility of sodium chlorate per unit volume of water or sodium chloride solution increases linearly with rise of temperature. The diminution produced in the solubility of sodium chlorate by addition of sodium chloride increases as the temperature rises, the extent of the increase being especially great for high concentrations of the chloride. Thermodynamic considerations indicate that the heat of solution of sodium chlorate in concentrated sodium chloride solutions should diminish as the temperature rises, and that the solubility of sodium chloride is diminished by addition of the chlorate more at high than at low temperatures. T. H. P.

Polychroism of Colloidal Sulphur. RUDOLF AUERBACH (*Kolloid Zeitsch.*, 1920, **27**, 223—225).—Colloidal sulphur is capable of exhibiting various colours depending on the degree of dispersion. The colour changes can be shown by adding phosphoric acid to sodium thiosulphate solution when first a weak turbidity appears, which is followed by a yellowish-blue opalescence, and then the colour observed by transmitted light passes slowly through yellow, green, red, violet, and blue, and finally the sulphur is precipitated. The whole process occupies twenty minutes. The following quantities are recommended for demonstration of the process: (i) For demonstration in a test-glass: 10 c.c. of $N/20$-sodium thiosulphate are treated with 0·1 c.c. of phosphoric acid (D=1·70) in 9·9 c.c. of water. (ii) For demonstration by lantern projection on a white screen: 15 c.c. of $N/20$-sodium thiosulphate solution are treated with 0·1 c.c. of phosphoric acid (D=1·70) in 4·9 c.c. of water. It follows, therefore, that disperse systems of dielectric substances can show polychromatic colours just in the same way as metallic disperse systems. J. F. S.

Preparation of Sulphur and Sulphuric Acid from Sulphates of the Alkaline Earths. E. H. RIESENFELD (*J. pr. Chem.*, 1920, [ii], **100**, 115—158).—I. *Reduction of Kieserite by Carbon*

[with ALFRED FABER].—A review of the literature on the utilisation of magnesium sulphate leads to preference being given to the proposal of Precht (*Chem. Ind.*, 1881, **4**, 350) to reduce kieserite by means of charcoal according to the equation $2MgSO_4 + C = 2MgO + 2SO_2 + CO_2$. Experiments showed that, at least in part, reaction occurs according to the equation $MgSO_4 + C = MgO + SO_2 + CO$. Thus the solid residue always contained sulphur when less than one atomic proportion of carbon to magnesium was employed, the best results being obtained with the proportion 1 : 1 at 750—850° or 1·5 : 1 at 950°. Under these conditions, the sulphur was obtained almost entirely as sulphur dioxide, with a little free sulphur. Contrary to what might be expected, reduction was not complete when greater proportions of carbon were used, probably because the molten sulphide then produced surrounded the sulphate and protected it from further action.

II. *Reduction of Gypsum and Anhydrite by Carbon* [with HANS FELD].—The reaction between gypsum and carbon sets in below 500°, but very slowly, and is fairly rapid from about 700° upwards. Under suitable conditions, pure calcium sulphide was obtained, approximately according to the equation $CaSO_4 + 3C = CaS + CO_2 + 2CO$. Similarly, from strontium and barium sulphates, the sulphides were produced, the different behaviour of magnesium sulphate being accounted for by a consideration of the heats of reaction. The composition of the gaseous phase in the former cases is controlled by the $C:CO:CO_2$ equilibrium, but in the case of magnesium sulphate this is disturbed by the action of sulphur dioxide on carbon monoxide.

III. *The Calcium Sulphate–Carbonate Equilibrium* [with (Frl.) ITALIENER and (Frl.) M. HESSE].—The equilibrium $CaS + H_2O + CO_2 \rightleftharpoons CaCO_3 + H_2S$ cannot be utilised for the disposal of calcium sulphide obtained by the above reduction, since at temperatures, for example, 700°, at which it is sufficiently rapidly attained, it favours the formation of calcium sulphide to a very considerable extent.

IV. *Reduction of Gypsum and Anhydrite by Gases* [with MARGARETE HESSE].—Gypsum was reduced by methane according to the equation $CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O$. Below 800°, dehydration of the gypsum alone occurred, but at 800—1000° quantitative reduction appears possible if the action be sufficiently prolonged. Above 1100°, some calcium oxide was produced, probably as a result of the reaction, $CaS + H_2O = CaO + H_2S$. The deduction from this equation that excess of steam would favour complete removal of sulphur was confirmed by experiments at 1200° and 1300°. Partly in consequence, however, of dissociation of hydrogen sulphide and partly by its reaction with water vapour (compare Randall and Bichowsky, A., 1918, ii, 159), the sulphur was obtained almost entirely as sulphur dioxide or elementary sulphur, the latter predominating when only a slight excess of water was employed.

V. *Decomposition of Calcium Sulphide by Steam and the Direct*

Conversion of Gypsum and Anhydrite into Oxide [with MARGARETE HESSE].—Experiments on the action of steam on calcium sulphide justified the assumption above of its intermediate formation, the amounts of sulphur dioxide and elementary sulphur produced being in agreement with the previous results. It must therefore be possible to convert calcium sulphate directly into the oxide by treatment with carbon and steam, and experiment showed this to occur at 1200°, but more than six times as rapidly at 1300°. Owing to the reducing action of carbon monoxide and hydrogen on sulphur dioxide, elementary sulphur predominated in the product, only 50% being obtained as the dioxide, even when 850 times the theoretical proportion of steam was employed. J. K.

Date of the Discovery of Tellurium and Bromine. PAUL DIERGART (*Zeitsch. angew. Chem.*, 1920, **33**, 299—300).—Tellurium was first discovered in 1782, or the beginning of 1783, by F. J. Müller of Hermannstadt; T. Bergmann of Upsala in 1783 concluded that a new element had been isolated. The element was discovered independently by Kitaibel in 1789, and the discovery was confirmed by Klaproth of Berlin in 1798, this investigator giving the name of "tellurium" to the element. Bromine had been isolated previous to 1826, but not recognised as a new element; it is mentioned by Bérard in a paper appearing in the *J. chim. Med.*, August, 1826; whilst Balard, *Ann. chim. phys.*, [ii], **32**, 337, August, 1826, gave the name "bromine" to the element. W. P. S.

The Reaction between Chlorine and Ammonia. II. WILLIAM A. NOYES and A. B. HAW (*J. Amer. Chem. Soc.*, 1920, **42**, 2167—2173. Compare A., 1901, ii, 601).—Anhydrous ammonia and anhydrous chlorine react to form nitrogen trichloride and ammonium chloride, $4NH_3 + 3Cl_2 = 3NH_4Cl + NCl_3$. A considerable proportion of the trichloride always decomposes into chlorine and nitrogen, either directly or by interaction between the trichloride and ammonia. The ratio of the number of molecules of chlorine to the number of molecules of ammonia may be varied between wide limits without affecting appreciably the ratio between the number of molecules of ammonia and the number of molecules of ammonium chloride. This ratio is 4 to 3. The chlorine reacts primarily with the ammonia, but only to a trifling extent, or not at all, with the solid ammonium chloride which is formed. The reaction was carried out with the dry substances without a solvent, and also in presence of carbon tetrachloride or pentane. J. R. P.

The Reaction between Chlorine and Ammonia. III. Probable Formation of Trichloro-ammonium Chloride. WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1920, **42**, 2173—2179).—Dry hydrogen chloride converts nitrogen trichloride quantitatively into ammonium chloride. The reaction may occur either in a solution of the trichloride in carbon tetrachloride or

without any solvent. This shows that the decomposition is not a hydrolysis, in the absence of water, and is probably not a hydrolysis in the presence of water.

The action probably consists primarily in the formation of trichloro-ammonium chloride, $\overset{+}{N}Cl_3H\overset{-}{Cl}$, followed by the loss of an atom of positive chlorine with an atom of negative chlorine. The formation of nitrogen trichloride by the action of chlorine on a solution of an ammonium salt appears to be the reverse of the above reaction. Ammonium sulphate is much more suitable than ammonium chloride for the preparation of nitrogen trichloride. Chloroamine and dichloroamine are formed, as well as nitrogen trichloride, by the action of chlorine on ammonium salts. Treatment of an ammonium salt with hypochlorous acid gives a trichloride pure and free from chloro-amines. Nitrogen trichloride may be separated from a solution, in which it is prepared, by a current of air, drying the air and vapour of trichloride by passing through concentrated sulphuric acid, and condensing the trichloride in a U-tube surrounded by a freezing mixture. J. R. P.

Reactions of Salts of Nitrous Acid with Weak Bases. K. A. HOFMANN and GUSTAV BUHK (*Ber.*, 1920, **53**, [*B*], 2165—2171).—It was shown in a previous paper (A., 1920, ii, 487) that carbon monoxide is oxidised by alkali hydroxides in contact with copper with formation of carbonate and free hydrogen, the latter being in the nascent form and having powerful reducing properties. Experiments are now recorded in which a strongly alkaline solution of sodium nitrite was used, but absorption of carbon monoxide was extremely slow. When ammonia was substituted for the strong alkali, absorption was again slow at first, but gradually became more rapid with formation of ammonium carbonate and a gaseous mixture of nitrous oxide, nitric oxide, and nitrogen. The accelerated reaction was found to be due to the formation of the hydrogen carbonate, and it was further found that a solution of sodium nitrite and ammonium hydrogen carbonate reacted with copper at ordinary temperatures with formation of a gas consisting of a mixture of nitrous oxide and nitrogen with very little nitric oxide. This reaction provides a convenient way of preparing nitrous oxide gas for laboratory purposes. Instead of ammonium hydrogen carbonate, ammonium chloride or sulphate can be used. Using 14 grams of sodium nitrite and 22 grams (two molecular proportions) of ammonium chloride in 200 c.c. of water, a total of 1025 c.c. of gas was obtained consisting of 81 c.c. of nitric oxide, 845 c.c. of nitrous oxide, and 99 c.c. of nitrogen. The greater part of the nitric oxide was evolved in the early part of the reaction, whilst the nitrogen content of the gas remained fairly constant throughout.

The reaction is due in the first place to the reduction by the copper of free nitrous acid formed by hydrolysis of ammonium nitrite (produced by double decomposition of the sodium nitrite and ammonium salt), $2HNO_2 + Cu = 2NO + Cu(OH)_2$. The cupric

hydroxide dissolves in the ammonia (a blue colour appears on the surface of the copper), and is reduced by copper to the cuprous form. The cuprous oxide then reduces the nitric oxide further to nitrous oxide, $2NO + Cu_2O = N_2O + 2CuO$. The free nitrogen must be formed by the normal decomposition of ammonium nitrite into nitrogen and water. Magnesium nitrite behaves in a similar manner with copper, but, since it is much less hydrolysed than ammonium nitrite, the reaction proceeds at only about one-sixtieth of the rate. E. H. R.

Transformation of Quartz into Tridymite. ORAZIO REBUFFAT (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 437—438).—The transformation of silica at 1300—1350° from the quartzose form into the form having the lower density, 2·22—2·27, which consists predominantly of tridymite, is facilitated by the presence of small proportions of phosphoric acid. T. H. P.

The Rare Gases of the Natural Gases of Alsace-Lorraine. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1920, **171**, 941—947).—The natural gases examined were from petroleum borings, a potash mine, a coal mine, and two mineral springs. The percentages by volume found for the rare gases were argon plus traces of krypton and xenon, 0·0104—1·01%; helium plus traces of neon, 0·0006—1·68%. The constant presence of nitrogen and of the five rare gases was shown in these natural gases of Alsace-Lorraine and, in all but one case, the constant absence of oxygen. The detailed analyses confirm results previously obtained as to the relative proportions of the various rare gases present in natural gases (compare A., 1916, ii, 389, 481). W. G.

The Action of Ozone on Alkali Metals, Ammonia, and Substitution Products of Ammonia. WILHELM STRECKER and HEINZ THIENEMANN (*Ber.*, 1920, **53**, [*B*], 2096—2113).—The action of ozone on solutions of the alkali and alkaline earth metals in liquid ammonia was investigated in the hope of elucidating the constitution of the products obtained by Traube (A., 1912, ii, 844) and others by the action of ozone on concentrated sodium or potassium hydroxide solutions. Although precipitates were obtained which appeared to be ozonides of potassium, sodium, rubidium, cæsium, calcium, and barium, these could not be obtained in a pure state on account of by-products formed by the action of ozone on ammonia. The compounds obtained were orange to brown in colour, readily decomposed by water or dilute acids with evolution of oxygen, and giving the hydrogen peroxide reaction with titanium sulphate solution. The ozonides of rubidium and cæsium are the most stable of those prepared.

Quantitative experiments on the action of ozone on liquid ammonia cooled in a carbon dioxide–ether mixture showed that the ozone was completely reduced, the products of the reaction being about 98% of ammonium nitrate and 2% of nitrite. When ozone is first passed into the liquid ammonia, an orange colour appears,

which may be due to the formation of an unstable ozonide. Carefully dried ozone at first acts very slowly on liquid ammonia, but as the reaction proceeds, the water formed has an accelerating influence.

Hydroxylamine hydrate reacts readily with ozone, hydroxylamine nitrate being the sole product of the reaction. The reaction is not complete, excess of ozone being required. Hydrazine hydrate is oxidised by ozone principally to nitrogen and water, only small quantities of hydrazine and ammonium nitrates being formed.

Methylamine and ozone react to form formaldehyde with ammonium and methylammonium nitrate and nitrite. Dimethylamine reduces ozone rapidly and completely, the reaction products identified being nitrate, nitrite, formaldehyde, and formic and acetic acids. The reaction between trimethylamine and ozone is explosive, even at the temperature of an ether–carbon dioxide mixture, and it was necessary to use a 5—10% solution of the base in chloroform to study the reaction. The product of the reaction was trimethylamine oxide, $O\colon NMe_3$, which was precipitated from the chloroform as the hydrochloride, the hydrochloric acid being formed by the oxidising action of ozone on chloroform. E. H. R.

The Action of Fluorine on Potassium Hydrogen Sulphate. E. BRUNNER (*Helv. Chim. Acta*, 1920, **3**, 818—824).—The fact that potassium fluoride has a strong accelerating effect on the electrolytic production of per-salts and hydrogen peroxide might perhaps be ascribed to the little-known oxidising action of fluorine. The author has therefore tested the action of this gas on a saturated solution of potassium hydrogen sulphate and finds that oxidation of the sulphuric acid does take place, but whether the product is persulphuric acid or not is uncertain.

An improved copper cell for the electrolysis of anhydrous hydrogen fluoride is described, and also a small apparatus for the analysis of readily decomposable fluorides by means of the volume of silicon fluoride produced when the sample is heated with dry glass powder and anhydrous sulphuric acid. J. C. W.

The Formation of Additive Compounds between 100% Sulphuric Acid and the Normal Sulphates of the Alkali Metals. JAMES KENDALL and MARY LOUISE LANDON (*J. Amer. Chem. Soc.*, 1920, **42**, 2131—2141).—The freezing points of systems containing sulphuric acid and anhydrous normal sulphates of potassium, sodium, ammonium, and lithium were determined from the eutectic points to 300°. The curves showed the existence of the following compounds, omitting compounds of undetermined composition:

With potassium sulphate—(*a*) $K_2SO_4,3H_2SO_4$, m. p. 91·5°. (*b*) K_2SO_4,H_2SO_4, m. p. 218·6°; exists in three modifications with transition points at 182° and 202°.

With sodium sulphate—(*a*) $2Na_2SO_4,9H_2SO_4$; unstable at m. p.

(60° by extrapolation), transition points to the two modifications of $Na_2SO_4,2H_2SO_4$ occurring at 57° and 58°. (*b*) $Na_2SO_4,2H_2SO_4$; exists in two modifications, both unstable at the melting points, transition to Na_2SO_4,H_2SO_4 occurring at 95° and 109°. (*c*) Na_2SO_4,H_2SO_4, m. p. 186°.

With ammonium sulphate—(*a*) $(NH_4)_2SO_4,3H_2SO_4$, m. p. 48°. (*b*) $(NH_4)_2SO_4,H_2SO_4$, m. p. 146·9°.

With lithium sulphate—(*a*) $Li_2SO_4,7H_2SO_4$, m. p. 13·6°. (*b*) $Li_2SO_4,2H_2SO_4$; unstable at m. p., transition to Li_2SO_4,H_2SO_4 occurring at 50°. (*c*) Li_2SO_4,H_2SO_4; unstable at m. p. (170·5° by extrapolation).

The results are in agreement with the law that the stability of an additive compound increases with the difference in character (that is, the positive or negative nature of the constituent groups) of its components. The salts in sulphuric acid are regarded as weak bases. J. R. P.

Disodium Hydrogen Phosphate Dodecahydrate. DALZIEL LLEWELLYN HAMMICK, HECTOR KENNETH GOADBY, and HENRY BOOTH (T., 1920, **117**, 1589—1592).

Colour Changes on Coagulating Sulphide Hydrosols. FRIEDRICH VINCENZ VON HAHN (*Kolloid Zeitsch.*, 1920, **27**, 172—175).—The colour changes brought about by coagulating silver sulphide sols by potassium chloride solutions have been studied. The colour change depends on the concentration of the potassium chloride, and it is only observed between definite fixed limits of concentration; thus with concentrations of potassium chloride below 60 millimols. per litre there is no change, and above 0·22 mol. the colour is always brownish-red. When 5 c.c. of 0·12*N*-potassium chloride are added to 5 c.c. of the silver sulphide sol, a dark yellow coloration appears after five minutes; with 0·14*N*-potassium chloride in similar circumstances a pale leaf-green; 0·16*N* gives an ice-blue colour, 0·18*N* gives blue, 0·20*N* gives violet, and 0·22*N* a dull green. The stability of the colloidal condition at the above-named stages is not great, and in three to four hours the colours become somewhat less intense, and the sol is precipitated. Similar colour effects were found when magnesium sulphate, aluminium sulphate, and hydrochloric acid were used instead of potassium chloride. J. F. S.

Reduction of Sodium Silver Thiosulphate by Hyposulphite. I. ALBERT STEIGMANN (*Kolloid Zeitsch.*, 1920, **27**, 249—254).—The reduction of silver sodium thiosulphate by sodium hyposulphite has been studied under a number of conditions. According to Jellinek (A., 1919, ii, 231), sodium hyposulphite decomposes in solution according to the equations $2Na_2S_2O_4 = Na_2S_2O_5 + Na_2S_2O_3$; $Na_2S_2O_5 + H_2O = 2NaHSO_3$. Consequently, solutions of hyposulphite become acid, and the formation of the reduction nuclei in the sodium silver thiosulphate mixtures is thereby greatly reduced. Starting with neutral and alkaline

mixtures of the two reacting solutions, it is shown that the reduction occurs much more rapidly in the alkaline solution than in the neutral solution, since the neutral solution becomes acid during the reaction, owing to the decomposition of the hyposulphite, as indicated above. The silver from alkaline solutions coagulates more rapidly than the blackish-blue silver from acid solutions, which sediments very slowly and yields a precipitate which is deep black in colour. The silver from alkaline solutions is greyish-black, and when rubbed on paper takes on a bronze appearance. The reduction occurs much more rapidly in the presence of a little potassium iodide than in alkaline solutions, and more rapidly still in alkaline solutions containing a little potassium iodide. In all cases, the reduced silver is at first colloidal, which rapidly coagulates. In the alkaline (soda) solutions, the sol remains yellowish-brown in colour until coagulation sets in, but in all other cases the sol becomes reddish-blue very rapidly. Similar reactions are described in the presence of gelatin. J. F. S.

Dispersoid and Colloid Chemistry of Gypsum. I. Wo. Ostwald and P. Wolski (*Kolloid Zeitsch.*, 1920, **27**, 78—92).—The colloidal processes occurring in the setting of burnt gypsum have been investigated by measuring the viscosity of suspensions at various periods of time after the preparation of the suspensions. This method is shown to be a very suitable one for the study of 4—5% suspensions of burnt gypsum. Such suspensions show a strong increase in the viscosity for the first half hour after their preparation. The time–viscosity curves have the shape of an **S**. The concentration of gypsum has a marked influence, in so far as the difference between the initial and final viscosities (hydraulic effect) increases extraordinarily rapidly with the concentration. Temperature plays an important part in the setting of gypsum; the viscosity shows that no setting is taking place at 60°, and very little at 37°, whilst at 0° the increase in viscosity, that is, setting, is very great. Grinding and ageing of the burnt gypsum have a marked effect on the viscosity curve. Freshly ground preparations show a greater hydraulic effect than unground and aged specimens. This is due to the influence of the degree of dispersity. It is shown that more highly dispersed specimens have a greater hydraulic effect than less highly dispersed specimens. The influence of additions of various substances on the setting has also been studied. Thus potassium chloride in concentrations up to $0{\cdot}2N$ accelerates the setting of gypsum, but eventually gives a smaller hydraulic effect than pure water. On the other hand, concentrated solutions of potassium chloride retard the setting of gypsum in suspensions. Acetic acid, $2N$, retards the setting, but gives a somewhat larger hydraulic end effect. Gelatin, 0·2%, and 20% alcohol completely stop the setting of gypsum. J. F. S.

Thallic Nitrite. G. Canneri (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 142—146).—Treatment of a suspension of thallium sesquioxide in water with liquid nitrous anhydride, and subsequent

evaporation of the solution, even in the cold under reduced pressure, yields, not thallic nitrite, but thallous nitrate. The latter is also obtained when solutions of thallic sulphate and barium nitrite are mixed in the cold, and the resulting liquid evaporated at low temperature. That thallic nitrite is capable of existence in solution, although it cannot be obtained in the solid condition, is shown by the results of estimations of the total thallium, the thallic thallium, the nitrous nitrogen and the total nitrogen, and by the fact that the nitrogen collected in the estimation of the nitrous acid contains free chlorine, this being liberated by decomposition of the thallic chloride formed from the thallic nitrite and the ammonium chloride added.

Treatment of aqueous thallic nitrite solution with alcohol yields a precipitate of the sesquioxide. In ethereal solution, thallic nitrite is far more stable, and the salt separates in the solid state on evaporation of the solvent; it could not, however, be analysed directly. Decomposition of thallic nitrite, with formation of thallous nitrate, takes place solely in accordance with the equation $Tl(NO_2)_3 \longrightarrow TlNO_3+N_2O_3$, neither intermediate reduction products nor thallous–thallic complex compounds being formed.

T. H. P.

Mercuric Azide. A. STETTBACHER (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1920, **15**, 211—212).—The extreme sensitiveness of mercuric azide, even under water, renders it unsuitable for practical purposes. With stringent precautions, it may be prepared on a laboratory scale as follows. A solution of 6·5 grams of sodium azide is decomposed with concentrated sulphuric acid, and the gaseous hydrogen nitride produced is passed into 10 grams of mercuric oxide in 200 c.c. of boiling water. The hot solution of mercuric azide is passed through a filter in a funnel provided with a hot-water jacket, and the filtrate is gently agitated with a wooden splinter during cooling to avoid formation of crystals exceeding 1 mm. in length, these being extremely sensitive. A crystalline mass of mercuric azide is thus obtained of not appreciably greater sensitiveness than silver fulminate. An alternative method consists in mixing concentrated solutions of sodium azide and mercuric nitrate; mercuric azide is precipitated from this mixture as a powdery mass, which is even less sensitive than lead azide, but can be converted into the highly sensitive form by solution and crystallisation. Although mercuric azide has the same molecular weight, and develops the same volume of gas on detonation, as mercuric fulminate, its "brisance" is twenty to thirty times as great.

W. J. W.

A Revision of the Atomic Weight of Aluminium. The Analysis of Aluminium Bromide. THEODORE W. RICHARDS and HENRY KREPELKA (*J. Amer. Chem. Soc.*, 1920, **42**, 2221—2232).—Aluminium bromide was synthesised from very pure bromine and the purest obtainable aluminium. It was digested three times in nitrogen at different temperatures, and fractionated

by distillation twice in nitrogen and twice in a vacuum. The residue was in each case discarded, as were two of the portions first volatilised.

The aluminium bromide was decomposed by water in such a way that the reaction occurred slowly, and the solution precipitated by a weighed amount of pure silver. The silver bromide was collected and weighed.

The close agreement of all the five analyses shows that the material used was very nearly, if not quite, homogeneous. In the final four analyses, 15·84201 grams of aluminium bromide required 19·22350 grams of silver for complete reaction, corresponding with an atomic weight for aluminium of 26·963 (Ag = 107·88; Br = 79·916). This agrees fairly well with Thomsen's value, 26·99, and modern evidence seems to show that the atomic weight of aluminium is really less, not more, than 27. The new value is distinctly nearer a whole number than the old one. J. R. P.

Swelling Phenomena with Fibrous Alumina. HEINZ VON ZEHMEN (*Kolloid Zeitsch.*, 1920, **27**, 233—235).—Fibrous alumina as prepared by Wislicenus (*Zeitsch. angew. Chem.*, 1914, **17**, 803) constitutes a reversible gel. On heating, the loss of water takes place stepwise between 100° and 200°, inasmuch as a definite percentage of water is lost at any given temperature; 6·5% is lost at 100°, a further 3% at 150°, and 2—3% at 200°; above 200° there is no further loss. On keeping in an open dish, practically the whole of the water is readsorbed in one day, and the small residue in four to five days. The maximum adsorption of water is 60%, and this amount is taken up in a few weeks by keeping the fibrous material in an atmosphere saturated with water vapour. In taking up water, swelling occurs; thus 1·97 grams of material dried at 200° had a volume of 5·60 c.c., and on keeping for three days in an atmosphere saturated with water vapour, it increased in weight to 3·12 grams and in volume to 6·30 c.c. The power of adsorption of Congo-red has been examined. It is found that the air-dried material containing 13% of water adsorbs relatively more Congo-red than the ignited material, whilst with the completely hydrated material the adsorption is still greater. The increased power of adsorption is attributed to the increase in the degree of dispersion of the adsorbent by swelling. J. F. S.

The Permeability of Glass to Iodine and Bromine Vapours. JAMES BRIERLEY FIRTH (T., 1920, **117**, 1602—1603).

Electrolytic Formation of the Alkali Salts of Ferrous and Ferric Oxides. G. GRUBE and H. GMELIN (*Zeitsch. Elektrochem.*, 1920, **26**, 459—471).—The electrolytic formation of sodium ferrite and sodium ferrate has been investigated. It is shown that when iron which has been rendered active by cathode treatment is anodically polarised by a low current density in a 40% solution of sodium hydroxide and in complete absence of air, it passes into solution in the bivalent condition as sodium ferrite, Na_2FeO_2. At

80°, with a current density of 0·166 amp./sq. dcm., 0·026 molecular solutions of this compound may be prepared. The anodic solution of iron in strong solutions of sodium hydroxide at high temperatures takes place in two stages; in the first stage, iron dissolves in the bivalent condition, whilst in the second stage it passes into solution in the sexavalent condition as ferrate, with simultaneous evolution of oxygen. Nowhere does iron pass into solution in the tervalent condition. The electrolytic formation of sodium ferrite can be brought about either by anodic oxidation of an alkaline solution of ferrous hydroxide or by the cathodic reduction of sodium ferrate. Both reactions take place on platinum electrodes. The equilibrium potential of iron against a sodium ferrite solution and that of platinum against mixtures of ferrite and ferrate have been measured, and from the results the concentration of the ferric ions in the latter solution and of the ferrous ions in the former solution have been calculated. The results show that a solution of ferrite is much more complex than an alkaline solution of ferrous hydroxide. The anodic solution of bivalent iron in 40% sodium hydroxide takes place at 80° at potentials ϵ_H $-0·84$ to $-0·82$ volt. At a slightly higher potential, ϵ_H $-0·8$ to $-0·7$, the oxidation process $2FeO_2'' + 2\oplus \rightleftharpoons Fe_2O_4''$ takes place. In 40% sodium hydroxide solution, the equilibrium potential of the process $Fe + 2\oplus \rightleftharpoons 2Fe^{\cdot\cdot}$ lies at ϵ_H $-0·86$ volt, whilst that of the process $Fe^{\cdot\cdot} + \oplus \rightleftharpoons Fe^{\cdot\cdot\cdot}$ lies at ϵ_H $-0·69$ volt, and that of the process $Fe^{\cdot\cdot\cdot} + 3\oplus \rightleftharpoons Fe^{\cdot\cdot\cdot\cdot\cdot\cdot}$ at ϵ_H $+0·55$ volt. Using the above values, the potential of the reactions $Fe + 3\oplus \rightleftharpoons Fe^{\cdot\cdot\cdot}$ and

$$Fe + 6\oplus \rightleftharpoons Fe^{\cdot\cdot\cdot\cdot\cdot\cdot}$$

have been calculated, and the values $-0·80$ and $-0·13$ volt respectively found. J. F. S.

Cause of the Instability of Nickel Steels; its Elimination. CH. ÉD. GUILLAUME (*Compt. rend.*, 1920, **171**, 1039—1041. Compare *ibid.*, 1899, **129**, 155).—From a study of the effect of the addition of manganese or chromium or carbon to nickel steels on the instability of such steels, it is shown that the cause of such instability is due to the presence of carbon, and the consequent formation of cementite, the slow transformation of which is capable of producing the phenomena observed. The stabilisation of nickel steels would thus be brought about by the absence of cementite. It is shown that the addition to nickel steels of metals, such as chromium, tungsten, or vanadium, which have an affinity for carbon greater than that of iron, in sufficient amount render such steels far more stable, but a very slight residue of cementite always remains. To arrive at complete stability, it seems necessary to add to the alloy an excess of the third metal. W. G.

Nickel Plating of Aluminium. A. MAZUIR (*Ann. Chim. anal.*, 1920, [ii], **2**, 335—336).—Aluminium may be plated with a compact adherent coating of nickel by scouring it with milk of lime, and, after thorough washing, immersing it in an acid bath

of a metallic chloride, preferably manganese or ferric chloride. Finally, it is subjected to a current of 2·5 to 3 volts and 1 to 1·5 amp. per sq. dcm. in a solution of nickel sulphate, the anodes consisting of sheet nickel. [See, further, *J. Soc. Chem. Ind.*, 1921, 13A.] C. A. M.

The Constitution of the Paramolybdates. S. POSTERNAK (*Compt. rend.*, 1920, **171**, 1058—1060).—Ammonium paramolybdate can be obtained in a crystalline form in the anhydrous state, and to it the constitution

$$(NH_4O)_3MoO(O\cdot MoO_2)_5O\cdot MoO(ONH_4)_3$$

is assigned. In addition, two new ammonium heptamolybdates intermediate between the para- and meta-molybdates have been prepared. *Triammonium heptamolybdate*,

$$(NH_4O)_3MoO(O\cdot MoO_2)_5O\cdot MoO_2\cdot OH,$$

is obtained by boiling a solution of ammonium molybdate with molybdic oxide. *Ammonium heptamolybdate*,

$$NH_4O(OH)_2MoO(O\cdot MoO_2)_5O\cdot MoO_2\cdot OH,H_2O,$$

is the crystalline crust formed by warming an ordinary solution of ammonium molybdate on a water-bath. W. G.

Preparation of Anhydrous Tin Tetrachloride. H. J. TAVERNE (*Chem. Weekblad*, 1920, **17**, 610).—The method employed by Hensgen (A., 1891, 1160) for the preparation of antimony trichloride is applied to tin. Chlorine which has been dried by passing through sulphuric acid and calcium chloride in succession is passed over granulated tin, contained in a tube about 40 cm. in length and 2 cm. in diameter, which is supported in an inclined position in an elementary-analysis furnace. The tube is connected at its lower extremity with an adapter piece, which fits through a cork in the neck of a distillation flask, the arm of which is connected to a calcium chloride tube. The chloride trickles down the tube, and collects as a yellow fluid in the flask, whilst the impurities in the tin remain behind in the tube. The chloride is afterwards redistilled, with the usual precautions. S. I. L.

Mineralogical Chemistry.

Flagstaffite, a New Mineral. F. N. Guild (*Amer. Min.*, 1920, **5**, 169—172).—A colourless, transparent, crystalline material was found in the radial cracks of pine-tree logs which had been buried for at least 500 years near Flagstaff, in Arizona. Drusy cavities contain well-developed orthorhombic crystals of prismatic habit, $a:b:c=1{\cdot}2366:1:0{\cdot}5951$. The material sublimes at the m. p. 99—100·5° as needles; it is readily soluble in warm alcohol

or benzene, from which it is re-deposited as crystals identical in form with the original ones. D 1·092. Material for analysis was re-crystallised from alcohol, after dissolving away associated yellow resin with ether. The results, C 66·21, H 11·55, O 22·24, agree with the formula C_4H_8O. The molecular weight, determined by the boiling-point method in benzene, is 210, requiring the formula $C_{12}H_{24}O_3$. This compound is near to colophonin ($C_{10}H_{22}O_3$). In its mode of occurrence it resembles fichtelite, but this contains no oxygen. L. J. S.

Naumannite from Idaho. EARL V. SHANNON (*Amer. J. Sci.*, 1920, [iv], **50**, 390—391).—Grains and nodules, formerly supposed to be argentite, are found in abundance embedded in clay in the De Lamar mine, Silver City, Idaho. The material is bluish-grey with metallic lustre and faintly shining grey streak. It is very sectile and malleable; fracture hackly and irregular (no cleavage); H 2½, D 6·527. Deducting clay and marcasite, analysis gave Ag 75·98, Se 22·92, S 1·10%. L. J. S.

Boulangerite, Bismutoplagionite, and Jamesonite. EARL V. SHANNON (*Proc. U.S. Nat. Museum*, 1920, **58**, 589—607).—Since the publication of his paper on mullanite (A., 1918, ii, 117), the author has become aware that the formula $5PbS,2Sb_2S_3$ was suggested for boulangerite by Sjögren in 1897, and he shows in detail that the old analyses of boulangerite can be adjusted to agree with this formula. The name mullanite is therefore withdrawn, and the materials previously described under this name are now re-described as boulangerite. The following new analyses of boulangerite also agree with the formula $5PbS,2Sb_2S_3$, and the materials have in common a brown tinge in their streak. I, fibrous, from the North Star mine, Wood River district, Idaho. II, fibrous, from the Independence mine in the same district. III, a soft mass of interlaced fibres from Peru. IV, massive and schistose, from Ober-Lahr, Germany. V, massive and schistose, from Przibram, Bohemia.

	Pb.	Ag.	Fe.	Sb.	As.	S.	Insol.	Total.
I.	55·52	trace	0·43	23·63	1·06	19·36	*	100·00
II.	53·79	trace	0·41	23·83	0·12	18·11	3·58	99·84
III.	54·34	trace	0·47	25·33	—	18·51	0·36	99·01
IV.	54·44	trace	—	24·55	—	18·98	1·50	99·47
V.	55·08	—	trace	24·38	—	18·65	1·10	99·21
VI.	40·77	7·40	0·46	30·61	—	20·81	—	100·80†

* 10·86 insoluble deducted. † Also Cu 0·75.

The description of bismutoplagionite repeats that previously published (A., 1920, ii, 324), it being added that the mineral is probably orthorhombic. Analysis VI is of "silver jamesonite" from the Poorman mine, Silver City district, Idaho. The material is light grey, almost silver-white, with reddish-brown streak, and is massive and fine-grained with only a suggestion of fibrous texture; it, however, passes into needles. These needles are very brittle,

indicating the presence of a perfect basal cleavage. The analysis gives the plumosite formula $2(Pb,Ag_2)S,Sb_2S_3$, and the mineral might be described as an argentiferous plumosite; but since the fibres are brittle, the silver is regarded as replacing iron, and the formula is written as $7(P_{4/5}[Ag_2]_{1/5})S,3\frac{1}{2}Sb_2S_3$ (compare A., 1907, ii, 700).

Fuller details are given of the naumannite from Idaho (preceding abstract). L. J. S.

A Graphic Method for the Comparison of Minerals with Four Variable Components Forming Two Isomorphous Pairs. E. S. SIMPSON (*Min. Mag.*, 1920, **19**, 99—106).—In the spinel-chromite series, the two pairs are MgO,FeO and Al_2O_3,Cr_2O_3, and the general formula is $(Mg,Fe)O,(Al,Cr)_2O_3$. The relative molecular preponderance of the components of each pair, stated as a percentage of the maximum, is given by the formulæ $x=100(m-f)/(m+f)$ and $y=100(a-c)/(a+c)$, where m, f, a, c represent the number of molecules of MgO, FeO, Al_2O_3, and Cr_2O_3 respectively. The values of x and y, calculated from a number of published analyses and from two new analyses (I and II), are plotted on rectangular co-ordinates. The four corners of the main square are occupied by the pure compounds, MgO,Al_2O_3 (spinel), MgO,Cr_2O_3 (here named picrochromite), FeO,Al_2O_3 (hercynite), and FeO,Cr_2O_3 (chromite). Sub-species and varieties of intermediate composition are divided off in symmetrical areas within this square. Analyses I and II are of ceylonite from serpentine at Namban, Western Australia; it is black (tawny-olive in thin section) and dense with microgranular structure.

	MgO.	FeO.	MnO.	Fe_2O_3.	Al_2O_3.	Cr_2O_3.	Total.	Sp. gr.
I. ...	13·65	17·45	0·26	3·80	42·09	22·76	100·01	4·12
II. ...	14·10	17·77	0·28	3·21	40·35	22·60	100·38*	4·04

* Incl. SiO_2 1·51, H_2O 0·56, from about 4% of included serpentine.

L. J. S.

Chromohercynite, a New Spinellide, from Madagascar. A. LACROIX (*Bull. Soc. franç. Min.*, 1920, **43**, 69—70).—Granular masses with shining black, vitreous lustre, D 4·415, were found with blocks of magnetite and concretionary limonite in the red earth of the gneissic region between Farafagana and Vangaindrano. The following analysis by Raoult gives the ratios

$$Cr_2O_3,FeO:Al_2O_3,(Fe,Mn)O:Al_2O_3,MgO=2:1:1.$$

Cr_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	SiO_2.	H_2O.	Total.
38·64	27·12	0·61	27·00	1·10	5·33	0·28	0·25	100·33

The formula may be written $FeCr_2O_4,(Fe,Mg,Mn)Al_2O_4$, representing a isomorphous mixture of chromite and hercynite in equal molecular proportions. The mineral contains more chromium and less magnesium than picotite. L. J. S.

Paternoite, a New Mineral of the Saliferous Stratum of Monte Sambuco in the Calascibetta Region (Sicily). F. MILLOSEVICH (*Atti R. Accad. Lincei*, 1920, [v], **29**, ii, 286—289).—The rounded, white nodules previously described (A., 1920, ii, 626) have D 2·11, *n* 1·47—1·48, and consist of minute, lamellar crystals of either the trimetric or monoclinic system. The mean composition is:

B_2O_3.	MgO.	K_2O.	Na_2O.	Cl.	SO_3.	H_2O.	Total.
66·02	10·93	1·08	0·36	2·35	1·06	19·16	100·96

The mineral consists essentially of a hydrated magnesium tetraborate, $MgO,4B_2O_3,4H_2O$, which the author names *paternoite*, carnallite and blödite being present as admixtures. T. H. P.

Minerals of the Melanterite and Chalcanthite Groups: Hydrous Manganese and Cobalt Sulphates. ESPER S. LARSEN and M. L. GLENN (*Amer. J. Sci.*, 1920, [iv], **50**, 225—233).—Dumps of sulphide ores (pyrites, copper-pyrites, and blende) at the Good Hope and Vulcan mines, Gunnison Co., Colorado, contain in many of the interstices a pale greenish-blue, columnar mineral of the melanterite group. Analysis of this (by M. L. GLENN) gave the formula $RSO_4,7H_2O$, with Zn : Cu : Fe = 100 : 98 : 19.

CuO.	ZnO.	FeO.	SO_3.	H_2O.	Insol.	Total.	Sp. gr.
12·37	12·89	2·14	28·78	42·61	1·11	99·90	2·02

This is named zinc-copper melanterite. On exposure to dry air it loses water, and passes into the pale blue, crystalline pentahydrate, which is called zinc-copper chalcanthite. In the same way, other minerals and substances of the melanterite group pass over into the chalcanthite group. Optical data are given in detail.

Optical data are also given for the several crystalline hydrates of cobalt sulphate and manganese sulphate. Ordinary blue, glassy cobalt sulphate is the hexahydrate; it alters on exposure to the air to the pink pentahydrate, and finally, in part, to the monohydrate. A solution of cobalt sulphate at 23° under reduced pressure yields the heptahydrate, at 45° the hexahydrate, and on the steam-bath the monohydrate. The ordinary pink, glassy manganese sulphate is the tetrahydrate; it alters on exposure to the nearly white monohydrate. A solution of manganese sulphate at 23° under reduced pressure yields the pentahydrate, at 45° the tetrahydrate, and on the steam-bath the monohydrate. L. J. S.

Descloizite from Portugal. ALFREDO BENSAUDE (*Bull. Soc. Portugaise Sci. Nat.*, 1920, **8**, 154—156).—This occurs as a crust of small, brown crystals with wad on limestone in the zinc mine of Perguiça, at Sobral da Adiça. Analysis by C. LEPIERRE gave:

V_2O_5.	As_2O_5.	PbO.	ZnO.	CuO.	MnO.	FeO.	H_2O.	Total.	Sp. gr.
22·32	0·11	61·77	12·10	0·28	0·74	0·22	2·30	99·84	6·00

The manganese is present as wad. Phosphate and chloride are

absent. This is the first record of a vanadate from Portugal, apart from a very doubtful one of carnotite. L. J. S.

The Age of the Autunites of Portugal. A. MUGUET and J. SEROIN (*Compt. rend.*, 1920, **171**, 1005—1006).—From a determination of the ratio radium/uranium in samples of Portuguese autunite, taking the value of this ratio for primary minerals as $3{\cdot}40 \times 10^{-7}$, the authors calculate the age of the autunite deposits in Portugal as 1250—1900 years. W. G.

Analytical Chemistry.

The Importance of Adsorption in Analytical Chemistry. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1510—1529).—See this vol., ii, 19.

A New Indicator Reagent for Acids and Alkalis. E. BABE and T. CABRERA (*Revista de agr., commercio y trabajo, Havana*, 1919, 537—539).—For the detection of the adulteration of milk by the addition of lye from wood ashes, a new indicator for acids and alkalis was found in the dried, blue blossoms of the butterfly pea (*Clitoria ternatea*, Linn.). Alcohol (90%) was the best solvent, although water may be used. In acid solution, the colour is a bluish-red, in neutral solution marine-blue, and in alkaline solution sky-blue. To show alkalinity in milk, the new indicator was found to be far more sensitive than phenolphthalein. It is also recommended for Kjeldahl and phosphoric acid titrations. It is interesting to note that in Cuba cases have been found where milk was diluted with lye of the same density (1·15), so that density measurements and the Babcock test would not disclose the adulteration. CHEMICAL ABSTRACTS.

Indication of the Acid and Basic Functions and their Estimation. I. M. KOLTHOFF (*Rec. trav. chim.*, 1920, **39**, 672—676).—To demonstrate the acid or basic function of a substance, even if the dissociation constant is very small, the method of indicators may be used, and at the same time the dissociation constant of the substance can be determined. The conductivity-titration method (compare A., 1920, ii, 49, 420, 421) is recommended for the estimation. W. G.

The Salt Error of Cresol-red. ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1920, **42**, 2160—2167).—In the determination of the hydrogen-ion concentration of salt water by a colorimetric method with cresol-red as indicator, it is necessary to make a correction

for the effect of the salt on the colour of the indicator. This correction has been determined with buffer solutions of borax and boric acid, without and with sodium chloride, and a table of corrections for use with the indicator is given. J. R. P.

The Estimation of the Hydrogen-ion Concentration by means of Indicators. L. MICHAELIS and A. GYEMANT (*Biochem. Zeitsch.*, 1920, **109**, 165—210).—On adding a solution of a certain hydrogen-ion concentration to a one-colour indicator, a coloration of a definite depth is obtained. By estimating colorimetrically the depth of the colour produced, it is possible to determine the hydrogen-ion concentration. The best conditions under which these estimations can be carried out are described, and the formula for calculating the results is given. S. S. Z.

A New Nephelometer and the Principles of Nephelometric Measurements. HANS KLEINMANN (*Kolloid Zeitsch.*, 1920, **27**, 236—241).—A new nephelometer is described, which depends on the measurement of the height of a Tyndall cone in two liquids, one of which is a standard, which produces the same intensity of illumination in a telescope. The apparatus consists of two glass tubes, each graduated to a suitable volume and containing the liquid for comparison; these tubes are placed side by side on a metal table before two shutters, which may be opened to any measured amount. Into the glass tubes two cylinders of polished glass just dip, and the light passing through these from the Tyndall cones illuminates the two halves of an optical system. The width of the shutter opening is then regulated until the two halves of the field are equally illuminated. The height of the Tyndall cone is controlled by the width of the opening of the shutters, and the intensity of illumination varies directly with concentration. Experiments with the instrument show that there is a strict proportionality between turbidity and concentration in the two tubes for the ratio 1 : 4 between the concentrations in the two tubes. The instrument is easy to work, and amounts of phosphoric acid (P_2O_5) down to 0·0005 mg. in 25 c.c. of solution may be estimated, using the strychnine–molybdic reagent, with an average error of 0·5%. The essential point which must be insured in all experiments is that the size of the particles in the turbid liquid is uniform. J. F. S.

Turbidity Standard of Water Analysis. P. V. WELLS (*Bureau of Standards, Sci. Paper* No. 367, 1920).—The usual standard employed is a water containing 100 parts per million of silica in such a state of fineness that a bright platinum wire 1 mm. in diameter is just visible when immersed at a depth of 100 mm. in the water. The standard is, however, untrustworthy, the variations from the average amounting in some cases to more than 50%. If the standard was prepared and distributed by some central authority, the error would be eliminated to a considerable extent, and it is not impossible that standard samples of dry, powdered

silica can be prepared sufficiently uniform in size of particle to be used directly. W. P. S.

The Titration of Potassium Iodide with Mercuric Chloride. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 836—842).—This method is employed for the analysis, amongst others, of Sirupus Iodeti ferrosi. The end-point is affected by the concentrations of the reagents, and corrections must be applied to obtain trustworthy results. The correction may be calculated without difficulty by applying the laws of mass action, since the complex salt, potassium mercuri-iodide, gives by dissociation mercuric iodide, which begins to separate as soon as its concentration is sufficient to give a saturated solution. By reason of this dissociation, mercuric iodide begins to separate before the equivalent amount of mercuric chloride has been added. By employing the value used by Auerbach and Plüddemann for the complex constant K, which governs the balanced action $HgI_4'' \rightleftharpoons HgI_2 + 2I'$, and the figure given by Morse for the solubility of mercuric iodide, a series of corrections may be calculated for any given concentration of the reagent solutions, and these are found to agree very closely with the figures determined by a series of titrations with known solutions.

The influence of temperature is found to be negligible, and foreign substances generally interfere but little, unless they enter into the formation of complex mercury salts. Thus sugar, alcohol, and sulphuric acid exercise no other effect than is naturally due to their presence as inert substances, whilst hydrochloric acid, and especially bromides and thiocyanates, exercise a very marked influence. S. I. L.

Microchemical Reactions of Iodic Acid. A. Bolland (*Compt. rend.*, 1920, **171**, 955—957).—A description is given of the appearance under the microscope of precipitates given by iodic acid with the following reagents: thallium nitrate, silver nitrate, barium chloride, strontium and calcium acetates, rubidium chloride, cæsium sulphate, rubidium cadmium chloride, potassium chloride, sodium acetate, ammonia, and manganous chloride. The first two reagents may be used to detect iodic acid at a dilution of 1 in 5000, the next one at a dilution of 1 in 2500, the next three at a dilution of 1 in 300, whilst with the remainder the dilution must not be more than 1 in 80, and preferably 1 in 20. W. G.

Gravimetric Analysis. XIV. Estimation of Sulphuric Acid in the Presence of Calcium, Phosphoric Acid, and Chromium. L. W. Winkler (*Zeitsch. angew. Chem.*, 1920, **33**, 287—288).—The results obtained in the estimation of sulphuric acid as barium sulphate are somewhat too low in the presence of calcium, owing to the precipitation of calcium sulphate. This error may be largely eliminated by dissolving the sulphate in 25 c.c. of 10% hydrochloric acid containing 0·5 gram of ammonium chloride, and adding 5 c.c. of 10% barium chloride, drop by drop,

to the boiling solution. The liquid is then diluted, again boiled, and left until next day before filtration. In the presence of phosphoric acid, some barium phosphate is precipitated. The method described above should be used, and a reduction of 1·1 mg. made from the dried precipitate or added to the ignited precipitate. Complete precipitation of sulphuric acid in the presence of chromium is effected by evaporating the filtrate and washings from the barium sulphate, dissolving the residue in 20 c.c. of hot water containing one or two drops of hydrochloric acid, separating the insoluble sulphate, and adding its weight to that of the original precipitate. C. A. M.

New Titrimetric Estimation of Hyposulphite. R. FORMHALS (*Chem. Zeit.*, 1920, **44**, 869).—The reduction of ferricyanide by hyposulphite is expressed by the equation $2K_3Fe(CN)_6 + Na_2S_2O_4 + 2H_2O = 2K_3NaFe(CN)_6 + 2H_2SO_3$, and the reaction can be utilised for the titrimetric estimation of the latter substance. About 0·5 gram of hyposulphite is dissolved in 50 c.c. of air-free water, and the solution is titrated with $N/10$-ferricyanide solution, with the addition of a few drops of ferrous ammonium sulphate solution as indicator, the end-point being determined by the formation of a permanent blue coloration of Turnbull's blue. The ferricyanide solution is preferably standardised by a preliminary titration with pure hyposulphite. G. F. M.

A Modification and Simplification of Kjeldahl's Method of Nitrogen Estimation. H. CITRON (*Deutsch. med. Woch.*, **46**, 655—656; from *Chem. Zentr.*, 1920, iv, 456).—A "Kjeldahl pear" is described by means of which the ammonia of the oxidised substance can be distilled and received automatically by placing the apparatus which contains it in a drying oven at 175°. S. S. Z.

The Comparative Estimation of the Total Nitrogen in Urine by the Methods of Dumas and Kjeldahl. W. MESTREZAT and (MLLE) MARTHE PAUL-JANET (*Compt. rend.*, 1920, **171**, 1019—1021).—Estimations of total nitrogen in the same samples of urine by Dumas's method and Kjeldahl's method indicate that there may be nitrogenous substances present in urine which are not estimated by Kjeldahl's method. Under certain conditions of medical treatment, the difference between the results obtained by the two methods may be as much as 10% of the actual value. W. G.

Estimation of Nitrogen in Nitrates and Nitrites by means of Copper–Magnesium Alloy. TH. ARND (*Zeitsch. angew. Chem.*, 1920, **33**, 296—298).—In order to prevent interference by other salts, the quantities of magnesium chloride solution and of copper–magnesium alloy prescribed in the method proposed previously by the author (A., 1917, ii, 504) should be increased to 50 c.c. and 5 grams, respectively. W. P. S.

The Estimation of Nitrites and Nitrates in Plant Tissue. W. H. STROWD (*Soil Sci.*, 1920, **10**, 333—342).—The plant tissue is extracted with cold water, and in one portion of the extract the total nitrogen present as nitrite and nitrate is estimated as ammonia after reduction with Devarda's alloy. Another portion of the extract is heated on a water-bath with an excess of aspartic acid for one hour, the nitrite thus being destroyed. The residual nitrate nitrogen is reduced with Devarda's alloy and estimated as ammonia. W. G.

The Estimation of very small Quantities of Arsenic in Urine, Blood, and other Body Fluids, and the Arsenic Balance in the Silver Salvarsan Treatment. HUGO ENGELSON (*Zeitsch. physiol. Chem.*, 1920, **111**, 201—222).—The principle of the method is based on the Ramberg-Sjöström method. The organic substance is decomposed by boiling with concentrated sulphuric acid and fuming nitric acid, and the residual nitrogenous compounds are removed by heating with ammonium oxalate. After adding water, hydrochloric acid, potassium bromide, and hydrazine sulphate, the arsenic is distilled over as the trichloride, which is received in water and titrated with potassium bromate. By employing this method, it was found that the best part of the arsenic of silver salvarsan injected in a patient remained in the body after sixteen days; only 26·6% of the total arsenic was recovered in the urine. S. S. Z.

Relation between certain Constants in the System CO_2 aq. -$CaCO_3$. A. MASSINK (*Pharm. Weekblad*, 1920, **57**, 862—866).—Values for the concentration of hydrogen ions in the system CO_2 aq.-$CaCO_3$ in equilibrium for various concentrations of HCO_3' are determined by two methods, the first using Tillman's formula, and the second a formula obtained on the lines followed by Kolthoff (*ibid.*, 1917, **54**, 986). Inaccuracies in working out his formula are ascribed to the latter, and a new equation, $[H^+]=2{\cdot}29\times10^{-3}[HCO_3]^2$, is arrived at by correcting these. The new formulæ give very concordant results, with a small constant difference. S. I. L.

The Calculation and Estimation of Active Carbonic Acid in Drinking Water. I. M. KOLTHOFF (*Chem. Weekblad*, 1920, **17**, 390—396).—Massink's criticism (preceding abstract) has led to a further re-examination of the whole subject. The known determinations of $lCaCO_3$ are reviewed, together with the figures given by various authors for the solubility of the different forms of calcium carbonate in water, with and without the presence of carbon dioxide. From the results, assuming dissolved calcium carbonate to be completely dissociated, and dealing only with the hydrolysis of carbonate to hydrogen carbonate, the values $[OH']=7{\cdot}7\times10^{-6}$ and $P_{OH}=5{\cdot}11$ are determined at 16°. From this it follows that the dissolved carbonate is hydrolysed to the extent of 57%. A determination of P_{OH} in a solution of pure

carbonate confirmed the figure 5·11. No true figures can be obtained for the solubility of calcium carbonate at the boiling point, since carbon dioxide is evolved by decomposition of the hydrogen carbonate produced by hydrolysis, hydroxide being formed. A determination of the hydroxyl-ion concentration after boiling gave $7{\cdot}7 \times 10^{-5}$, a value ten times greater than that found for the solution before boiling.

The table of Tillmans and Heublein for the solubility product of calcium carbonate in presence of free carbon dioxide is held to be inaccurate. From the author's expression for the concentration of carbon dioxide in mg. per litre, $\alpha^3(\text{combined } CO_2)^3 \times 3{\cdot}44 \times 10^{-5}$, where α is the degree of dissociation of the calcium hydrogen carbonate, a new series of values is given, α being based on the conductivity measurements of Kendall.

A series of measurements of the solubilities of powdered marble in solutions containing various quantities of carbon dioxide was carried out, the solutions being prepared by shaking for several days at normal temperature; carbon dioxide was estimated in 100 c.c. after decantation by addition of ten drops of 1% phenolphthalein, and titration with $N/10$-sodium hydroxide until the rose coloration persisted for five minutes, whilst the hydrogen carbonate was determined in another 100 c.c. by titration with $N/10$-hydrochloric acid in presence of dimethyl-yellow. In the titration of the carbon dioxide, corrections must be introduced, since the amount of sodium hydroxide required in presence of phenolphthalein is found to be less than the amount equivalent to the carbon dioxide actually present; a table of the empirical corrections employed is given. The figures agree fairly well with the theoretical for values for combined carbon dioxide up to 100 mg. per litre; the experimental values are less than the calculated, and these, again, less than the values deduced from the table of Tillmans and Heublein. The table of these authors applies, in fact, only to systems in which the concentration of calcium is equal to that of hydrogen carbonate, which in practice is seldom the case in drinking-water, since this has usually some permanent hardness. A new table is accordingly given, the values for active carbon dioxide being directly determined by Heijer's method, and the figures deduced from the equation

$$[CO_2] = (\alpha^3[HCO_3]^2 \cdot \tfrac{1}{2}[Ca^{\cdot\cdot}])/(1{\cdot}13 \times 10^{-4}).$$

The table permits the calculation of the active CO_2 when the concentrations of HCO_3', CO_2, and $[Ca^{\cdot\cdot}]$ are known. S. I. L.

Perchloric Acid as a Dehydrating Agent in the Estimation of Silica. H. H. WILLARD and W. E. CAKE (*J. Amer. Chem. Soc.*, 1920, **42**, 2208—2212).—The silica in metals and silicates can be rendered insoluble by boiling with concentrated perchloric acid solution (60 to 70%) for a short time. Less silica remains in the filtrate than by the usual method of evaporating the hydrochloric acid solution to dryness, and the process is far more rapid. The perchlorates formed are dissolved instantly on dilution with

water, leaving pure silica uncontaminated by sparingly soluble salts. J. R. P.

Volumetric Estimation of Potassium and its Application to the Analysis of Fertilisers. GUIDO AJON (*Giorn. Chim. Ind. Appl.*, 1920, **2**, 422—426).—This method consists essentially in precipitating the potassium as potassium hydrogen tartrate in presence of alcohol, washing the precipitate repeatedly by decantation with 96% alcohol, adding $N/10$-sodium hydroxide solution in 96% alcohol until the reaction is alkaline, dissolving the precipitate in aqueous $N/10$-sodium hydroxide solution, and determining the excess of the latter by titration. [See *J. Soc. Chem. Ind.*, 1921, 21A.] T. H. P.

The Composition of Potassium Platinichloride. A. VÜRTHEIM (*Chem. Weekblad*, 1920, **17**, 637—640).—In the estimation of potassium as platinichloride, it has been found that the composition of the salt does not correspond with that required by the formula K_2PtCl_6. In view of the various factors suggested by different workers on the subject, the matter has been re-examined.

For the preparation of the double salt, dilute solutions of the two pure salts were used, in order to avoid the difficulties introduced in drying by enclosed mother liquor, where the solutions are too strong. The solution was then evaporated at 90° until it became syrupy, the crystals being washed free from platinic chloride with 96% alcohol. Drying for two hours at 150° was found to give constant weights.

By using a constant quantity of the potassium chloride solution with a slight excess of platinum chloride, practically constant yields of the double salt were obtained. Platinum and chlorine were determined in each sample, the potassium being known from the quantity of potassium chloride solution taken. The mean of six concordant determinations gave K : Pt : Cl = 15·98 : 40·32 : 43·16, the formula K_2PtCl_6 requiring, using the latest atomic weights, 16·09 : 40·15 : 43·76.

Quantities of the double salt were recrystallised and dried under various conditions, and it was found that by precipitation from aqueous solution by means of alcohol, the salt was obtained absolutely free from water, drying at 110° being as effective as drying at 150° in arriving at constant weights. The compound so treated gave on analysis K : Pt : Cl = 16·09 : 40·63 : 43·51, which, although much nearer to the theoretical than the above results, still shows some deviation. The accuracy of the accepted atomic weight of platinum is questioned, and the variations in this constant, as accepted in the last twenty years, are pointed out. S. I. L.

Estimation of the Alkali Metals as Sulphates. N. SCHOORL and I. M. KOLTHOFF (*Chem. Weekblad*, 1920, **17**, 425—427).—Van Duin's conclusions (A., 1920, ii, 508), that in the conversion of pyrosulphate to normal sulphate by ignition with addition of

ammonium carbonate, errors are introduced, (*a*) by the presence of unburned carbon (especially in the case of alkali salts of organic acids), and (*b*) by the loss of alkali sulphate with the volatile ammonium salts in the ignition, are investigated, and shown to be inaccurate. All residual carbon is destroyed by repeated heating with strong sulphuric acid in a closed crucible, care being taken not to evaporate off the acid too quickly. If, after this, the colourless pyrosulphate residue be further strongly heated, it solidifies on the walls of the crucible, disengaging sulphur trioxide. If a fragment of ammonium carbonate is added while the crucible is kept at this temperature, it does not volatilise violently, but assumes a condition analogous to the spheroidal state, and disappears slowly and quietly. This course gives accurate results.

The method suggested by van Duin, evaporating the pyrosulphate with ammonium carbonate solution and igniting the residue, is open to many objections; thus, alkali carbonates are formed in the solution, and the tendency to spitting is not diminished, but increased, because the crystals formed as the solution is evaporated enclose mother liquor. S. I. L.

Quantitative Analysis. XV. Estimation of Barium as Barium Sulphate. L. W. Winkler (*Zeitsch. angew. Chem.*, 1920, **33**, 299).—To 200 c.c. of the neutral solution containing the barium salt are added 1 gram of ammonium chloride and 1 c.c. of *N*/1-hydrochloric acid, the mixture is boiled, and a slight excess of 5% ammonium sulphate solution is added. After eighteen hours, the precipitate is collected, washed, dried, and weighed. For a quantity of about 0·3 gram of barium sulphate, 1·6 mg. is deducted from the weight of the dry precipitate; if the precipitate is ignited before being weighed, 0·6 mg. is added to the weight found. W. P. S.

The Volumetric Estimation of Barium and Strontium as Chromates. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 972—979).—The procedures given in the literature for the estimation of barium and strontium together, and in the presence of calcium, by the chromate method, and especially the work of van der Horn van den Bos (A., 1911, ii, 228), have been investigated with the view of obtaining accurate and trustworthy methods. In the absence of strontium, the presence of calcium having no effect on the estimation, barium may be determined by precipitation with excess of dichromate at the ordinary temperature in presence of a little acetate. After three hours, the precipitate is filtered off, and the excess of dichromate in the filtrate estimated iodometrically. If strontium is present, appreciable quantities will be thrown down with the barium by this method, but accurate results may be obtained by the following procedure. To 10 c.c. of the solution are added 10 c.c. of 4*N*-acetic acid and 10 c.c. of 2*N*-sodium acetate, with 20 c.c. of water. Slight excess of dichromate is added, the whole made up to 100 c.c., and filtered

after three hours. Fifty c.c. of the filtrate are treated with iodide, and the iodine liberated determined with thiosulphate.

For the estimation of strontium, after addition of the dichromate, pure ammonia is added until the solution is just yellow, and the strontium chromate precipitated with absolute alcohol, the excess of chromate being determined in an aliquot part of the filtrate, as before. In the presence of barium, the results are always low. Although the barium may be quantitatively estimated first by precipitation, and estimation of the chromate in an aliquot part of the filtrate, addition of ammonia and alcohol to another part of the filtrate (the procedure which gives good results for strontium alone) seems not to precipitate the strontium completely, the results being about 2% too low. This is attributed to the large amounts of acetate required. The presence of calcium also makes the method inaccurate, more than 100 mg. per litre causing serious errors. S. I. L.

The Separation of Barium, Strontium, and Calcium by the Chromate Method. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 1080—1084).—The three elements can be satisfactorily separated qualitatively by the chromate method by the following procedure. The group IV carbonate precipitate is dissolved in dilute acetic acid, and the solution boiled to remove carbon dioxide. Sodium acetate is then added until its molecular concentration is equal to that of the acid, and the barium precipitated with a slight excess of dichromate. After five minutes, the precipitate is filtered off, and the filtrate made faintly alkaline with ammonia. Addition of an equal volume of rectified spirit, with more chromate if necessary, throws down the strontium, which is filtered off after half an hour. Calcium is detected in the filtrate by means of ammonium oxalate.

The precipitate from the alcoholic solution must be tested to confirm strontium, since acidity of the original solution will prevent complete precipitation of the barium, the last traces coming out of solution when ammonia and spirit are added; also, if the ammonia contains carbonate, some calcium may be thrown down. The precipitate may be tested by the flame reaction or the spectroscope, or may be washed with 50% alcohol, dissolved in hydrochloric acid, and the strontium thrown down as sulphate. One mg. of strontium can be detected in presence of 100 mg. of barium and 100 mg. of calcium per litre. The procedure will also detect 1 mg. of barium in presence of 100 mg. each of strontium and calcium; it is so sensitive for calcium that 0·1 mg. per litre can be detected in presence of 100 mg. each of barium and strontium.
S. I. L.

Estimation of Lead as Chromate. C. W. Simmons, J. R Gordon, and H. C. Boehmer (*Canad. Chem. J.*, 1920, **4**, 139).—The following procedure is recommended for the volumetric estimation of lead in ores. A suitable amount of the ore is dissolved in a mixture of hydrochloric and nitric acids, the solution evaporated

to a volume of 8 c.c., a slight excess of ammonia is added, and then an excess of acetic acid. If the solution is not clear, 3 grams of ammonium acetate may be introduced. Ten c.c. of 10% potassium chromate are then added, the mixture is kept warm for five minutes, and the precipitate collected. The precipitate is dissolved in a mixture of 25 c.c. of concentrated hydrochloric acid and 75 c.c. of water, the solution diluted to 200 c.c., slightly less than 1 gram of potassium iodide is added, and the liberated iodine is titrated slowly with thiosulphate solution. W. P. S.

Titration of Lead as Lead Chromate. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 934—941).—The various methods of applying the volumetric chromate method to the estimation of lead have been examined, and the method involving the use of iodine and thiosulphate is found to give the best results. For rapid estimations of small quantities, it is simplest to estimate the chromate in the washed lead chromate precipitate by dissolving this in dilute hydrochloric acid, adding excess of potassium iodide, and titrating the liberated iodine with thiosulphate. The difficulty that lead chromate separates to a large extent in the colloidal form may be overcome by adding a few drops of a 5% aluminium chloride solution, and by heating and shaking after addition of the chromate solution. The precipitate is collected on a cotton-wool filter, washed until free from soluble chromate, and transferred again to the flask in which it was thrown down, since particles of the precipitate are found to adhere to the walls. With experience, a complete determination can be carried out in fifteen minutes, the method giving very satisfactory accuracy. Where very low concentrations and small quantities of lead have to be determined, it is advisable to allow the precipitate to remain overnight, the solubility of lead chromate being found to be negligible.

The method is very suitable for the estimation of lead sulphate, which may be dissolved in sodium acetate with addition of a little acetic acid, and the solution treated with chromate, as above.

For high concentrations of the lead salt (up to one-twentieth molar solutions), accurate results may be obtained by titrating the excess of chromate with iodine and thiosulphate. Since the chromic acid liberated in the reaction $PbAc_2 + K_2Cr_2O_7 = CrO_3 + 2KAc + PbCrO_4$ functions as a strong monobasic acid, the determination may also be carried out by measurement of the conductivity changes when the reaction liquid is titrated with sodium hydroxide. The conductivity falls rapidly until all the chromic acid has been converted into dichromate, after which it rises slowly as the chromate is formed. This modification can, naturally, only be used where the lead is in the form of a salt of a strong acid.

S. I. L.

The Separation of Mercury from other Elements by Distillation from Hydrochloric Acid Solution. WILHELM STRECKER and KARL CONRADT (*Ber.*, 1920, **53**, [*B*], 2113—2127). —In a previous paper (A., 1920, ii, 51) on the separation of

antimony from tin by volatilising from a hydrochloric acid solution, it was observed that mercury is also partly volatilised under similar conditions. Experiments have now been made to determine the conditions under which mercuric chloride can be completely volatilised from solution. By leading a current of hydrochloric acid gas through an aqueous solution of mercuric chloride at 110°, only very small quantities of mercury distilled over. Better results were obtained by dissolving the mercuric chloride in concentrated sulphuric acid and dropping concentrated hydrochloric acid into the solution while a current of the gas was passed through at 170—180°. When, in place of the concentrated hydrochloric acid, a mixture of this with 10% of hydrobromic acid was dropped in, the whole of the mercuric chloride was distilled over in half an hour at 160—170°. By dropping in the aqueous acid during the distillation, the accumulation of the mercuric chloride on the walls of the distillation vessel was prevented, and consequently the distillation was accelerated. Phosphoric acid, it was found, could be used in place of sulphuric acid, and in this case no advantage was found when hydrobromic acid was used with the hydrochloric acid. It was subsequently found that the stream of hydrochloric acid gas could be dispensed with, and a current of air or nitrogen used instead. From phosphoric acid solution, the mercuric chloride could be completely distilled over in one hour at 150—160° by slowly dropping water into the solution. Mercuric bromide was found to be much less volatile than the chloride.

By the distillation process, mercury can be readily separated from many other elements, copper, cadmium, iron, and the other elements of the ammonium sulphide group, barium and other alkaline earth elements. In the case of lead, if sulphuric acid is used for the distillation, the lead sulphate may enclose some of the mercuric chloride, and it is better to use phosphoric acid. The separation from bismuth is not complete, as the chloride of this element is volatile to some extent. E. H. R.

Electro-analytical Practice. W. Böttger (*Zeitsch. Elektrochem.*, 1920, **26**, 445—452).—The author has examined the causes of the low results obtained in the estimation of mercury by electrodeposition. It is shown that mercury is quantitatively deposited from mercurous nitrate solutions in the presence of nitric acid when a constant *E.M.F.* of 1·4—1·5 volts is employed. When mercuric nitrate is used, the solution should be acidified with 1 c.c. of nitric acid (D 1·4). The *E.M.F.* is so regulated that the current strength remains at 1 ampere. To ensure this, the electrolysis is commenced with an *E.M.F.* of 1·8 volts, which rises to 3·0 volts in about four minutes, and finally reaches 3·2—3·3 volts, at which value the electrolysis is completed. The conditions for electrolysis in the presence of potassium cyanide are also given. The reasons for the loss so very often experienced and the amount of the loss are discussed. It is shown that pure alcohol and pure ether may be used for drying the deposit if the electrode is only

exposed to the air for a short time (ten to fifteen minutes). Losses due to keeping in a desiccator are vanishingly small. Losses due to loosening of particles of mercury, and washing away when wet electrodes are dipped into alcohol, are very small and approximately constant. The losses, in the estimation of acid solutions of the nitrate, using an *E.M.F.* of 1·4 or 1·5 volts, or of chloride solution, to which 1 c.c. of nitric acid (D 1·4) has been added, with an *E.M.F.* of 1·8—3·3 volts, amount to 0·4 mg. when a silvered net electrode is used. Separation from a cyanide solution gives slightly larger losses, 0·6 mg. The cyanide method is doubtful only when a large amount of potassium cyanide is present and when large currents are used. J. F. S.

The Analysis of Mercuric Chloride. I. M. Kolthoff and J. Keijzer (*Pharm. Weekblad*, 1920, **57**, 913—919).—The method of Rupp for the estimation of mercuric chloride by reduction with formalin in warm alkaline solution, and estimation of the mercury so formed by treatment with excess of iodine in acid solution and back titration of the excess with thiosulphate, is found to give variable results. The variations are traced to two causes. The reduction in alkaline solution by means of formalin is not complete, some calomel being formed. The second source of error arises from the fact that although neither formalin nor its common impurities react with iodine, after warming with sodium hydroxide and subsequent acidification, as in Rupp's method, formalin is found to combine slowly with iodine, probably on account of the polymerising effect of the alkali.

A more accurate form of the method is found to be the use of alkaline hydrogen peroxide for the reduction, with subsequent acidification with sulphuric acid, the estimation being completed as before. Since the reduction requires fifteen minutes on the water-bath, with constant shaking, whilst it requires another thirty minutes to dissolve the separated mercury in iodine, the method is somewhat laborious.

A more satisfactory method is suggested on the basis of the work of Andrews (A., 1903, ii, 695), who found that the addition of pure hydrocyanic acid to a solution of mercuric chloride gave a strongly acid solution, on account of the very slight dissociation of mercuric cyanide. To the neutral mercuric chloride solution is added a slight excess of hydrocyanic acid solution (prepared from potassium cyanide and hydrochloric acid), which reacts neutral to dimethyl-yellow. The mixture is then titrated directly with sodium hydroxide, using the same indicator. The method gives very good results in all concentrations, but care must be taken that the solutions are neutral, and the hydrocyanic acid must be free from cyanic acid, which, being a relatively strong acid, introduces errors. S. I. L.

Analysis of Gold. H. Wolff and N. Singalowsky (*Zeitsch. angew. Chem.*, 1920, **33**, 298).—A criticism of a method described recently by Drawe (A., 1920, ii, 775). Older and better known

methods yield trustworthy results for the separation of silver and copper from gold; in Drawe's method there is the risk that silver and copper are not removed completely by a single precipitation.

W. P. S.

Estimation of the Phenolic Substances in Urine. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1920, **44**, 409—427).—The values obtained by the method of Folin and Denis for the estimation of phenolic substances in urine (A., 1915, ii, 802) are as much as 50% higher than those which are obtained with the ether extraction method outlined in this paper. This suggests that there are unidentified substances present in urine which react with the colour reagents used by Folin and his collaborators, and are responsible for the high values obtained by the former method.

These unidentified interfering substances are partly present in the urine in the free state and partly formed by the action of strong mineral acids on the urine. Only a small fraction of the volatile phenols is excreted in the urine in the free state.

J. C. D.

Micro-estimation of Dextrose by Bang's Method. ALBRECHT MERTZ (*Zeitsch. physiol. Chem.*, 1920, **111**, 43—48).—By employing Bang's improved micro-method for the estimation of dextrose, a uniform reduction factor was obtained with quantities of 0·06—0·4 mg. of dextrose. The iodate solution employed in the estimation is stable if pure reagents are employed.

S. S. Z.

Estimation of Dextrose and Starch by the Alkaline Permanganate Method. FRANCISCO A. QUISUMBING (*Philippine J. Sci.*, 1920, **16**, 581—601).—The author has studied the influence of the concentration of the reacting substances, and the conditions of heating, on the oxidation of dextrose by potassium permanganate in presence of sodium carbonate. A method of procedure is described which can be applied to the estimation of dextrose; the excess of permanganate is determined by means of standard oxalic acid solution, and from the volume of permanganate reduced the amount of dextrose present is found by reference to a table. The method can be used for the estimation of starch in commercial starch after hydrolysis by acid or diastase, or in flours after hydrolysis by saliva or diastase but not after hydrolysis by acid.

J. H. L.

The Double-polarisation Method for the Estimation of Sucrose and the Evaluation of the Clerget Divisor. RICHARD F. JACKSON and CLARA L. GILLIS (*Bureau of Standards, Sci. Paper* No. 375, 1920).—The velocity of inversion of sucrose between 20° and 90° follows the exponential law first proposed by Arrhenius. From the rate of decomposition of invert-sugar in the presence of hydrochloric acid at different temperatures, it is

concluded that, for the Clerget method, 50° is the most satisfactory temperature. The value of the rotation, multiplied by 2, of 13 grams of sucrose in 100 c.c., inverted and polarised in the presence of 6·34*N*-hydrochloric acid, is $-33{\cdot}25°$ at 20°, and not $-32{\cdot}66°$, as given by Herzfeld; the basic value of the Clerget divisor is 143·25, and not 142·66. The presence of hydrochloric acid increases the lævorotation of invert-sugar; if *C* is the number of c.c. of 6·34*N*-hydrochloric acid per 100 c.c., the rotation, *R*, of invert-sugar is $R_T^{20} = -32{\cdot}00 - 0{\cdot}125C$. The effect of hydrochloric acid can be duplicated by normal salts, such as sodium chloride, potassium oxalate, and calcium chloride, and it is proposed to add 2·315 grams of sodium chloride to the solution for direct polarisation to secure a constant rotation of invert-sugar when it exists as an impurity. Four methods of analytical procedure are given, and the values of the Clerget divisor are tabulated in convenient form. W. P. S.

Technique of the Estimation of Lactic Acid and the Determination of the Maximum Capacity of Lactic Acid Formation of the Muscle. GENIA RIESENFELD (*Biochem. Zeitsch.*, 1920, **109**, 249—270).—The extraction of lactic acid with amyl alcohol according to Ohlson's method yields satisfactory results when aqueous solutions are employed, but not when the solutions contain protein. In the case of muscle extracts, the author therefore recommends the precipitation of the protein with phosphotungstic acid. When the solutions are boiled, a small and negligible quantity of the lactic acid is retained by the coagulum. In order to estimate the maximum lactic acid formation in muscle, the author recommends autolysing the minced organs under an antiseptic for three days, in order that the lactacidogen may pass into lactic acid. The presence of the lactic acid anhydride must be taken into consideration. S. S. Z.

Naphthalenesulphonic Acids. II. Detection of certain Naphthalenesulphonic Acids. JOSEPH A. AMBLER and EDGAR T. WHERRY (*J. Ind. Eng. Chem.*, 1920, **12**, 1085—1087).—The characteristics of the ferrous and naphthylamine salts of certain naphthalenesulphonic acids (this vol., i, 21) may be used for the detection of those acids in the mixed products of the sulphonation of naphthalene. The sulphonic acids are converted into sodium salts, and the solution tested with ferrous chloride, a precipitate indicating the 2-sulphonic acid. The boiling filtrate, treated with α-naphthylamine hydrochloride, will give a precipitate in the presence of the 1:5-disulphonic acid, whilst the 2:6-disulphonic acid may be detected in the filtrate from this by means of β-naphthylamine hydrochloride. The salts separated from the filtrate from the 2:6-disulphonate are extracted with acetone to separate β-naphthylamine naphthalene-α-sulphonate, whilst the 2:7- and 1:6-disulphonates are identified by their optical behaviour. [See also *J. Soc. Chem. Ind.*, 1920, 815A.] C. A. M.

The Quantitative Estimation of Acetone and Acetaldehyde in the same Solution. WILHELM STEPP and WILHELM ENGELHARDT (*Biochem. Zeitsch.*, 1920, **111**, 8—17).—Ripper's method for the estimation of acetone and acetaldehyde in mixtures (A., 1907, ii, 205) was found to be suitable provided that at least forty hours are allowed for the reaction to take place. Results obtained in the estimation of acetone and acetaldehyde in mixtures with the iodoform method were unsatisfactory. S. S. Z.

Reaction of "Saccharin." L. THEVENON (*J. Pharm. Chim.* 1920, [vii], **22**, 421—422).—A bright red coloration is obtained when 0·1 gram of "saccharin" dissolved in 25 c.c. of water is treated with 10 c.c. of 0·1% sodium nitrite solution, 6 drops of dilute sulphuric acid, and, after a few minutes, 0·1 gram of β-naphthol. W. P. S.

Detection of very small Quantities of Indican (Potassium Indoxyl Sulphate) in Water as an Aid to Hygienic Water Analysis. ADOLF JOLLES (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 421—442).—The presence of the merest traces of indican in a water is a certain indication of previous contamination with animal excretions, and as its detection by chemical means is very simple and not interfered with by the commonly occurring constituents of natural waters excepting nitrites, which, however, are readily eliminated by means of ferrous salts, its presence or absence forms an excellent criterion for the judgment of a water from the hygienic point of view. The test is performed as follows: 3 to 4 litres of the water are evaporated to 250 c.c., and if nitrites are present 3 grams of ferrous ammonium sulphate are added for every 0·1 gram of nitrite per litre of the original water. The evaporation is then continued to 10 c.c., and to the filtered solution 1 c.c. of 5% alcoholic thymol or α-naphthol solution and 10 c.c. of fuming hydrochloric acid containing 5 grams of ferric chloride per litre are added. After keeping for fifteen minutes with frequent shaking the indolignone colouring matter, which will have been formed if indican were originally present, is extracted by careful shaking with 4 c.c. of chloroform. A reddish- or bluish-violet coloration of the chloroformic layer, however slight, is a certain proof of the presence of indican, and of the previous contamination of the water with animal excreta. G. F. M.

Differentiation of the Extract of Yellow Wood (Morin) and the Extract of Quercitron (Quercitrin). ED. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1920, [iv], **27**, 844—846).—The extract of these two woods may readily be distinguished from one another by dissolving a trace of extract, either dry or the concentrated solution, in sulphuric acid (D 1·817), and then diluting with water. Under these conditions, the extract of yellow wood remains bright orange-yellow, whilst the extract of quercitron is decolorised. A microscopic examination of the two extracts also serves as a means of differentiation. That of quercitron appears in more or less agglomerated granules, whilst that of yellow wood shows sharply defined crystals. W. G.

Apparatus for the Estimation of Small Quantities of Urea. A. J. L. Terwen (*Nederl. Tijdschr. Geneeskunde*, 1920, **64**, ii, 875—880; from *Chem. Zentr.*, 1920, iv, 638).—The estimation of urea by bromine and sodium hydroxide is liable to error, since ammonium salts, creatine, uric acid, and hydroxyproteic acids can also yield nitrogen under these conditions, whilst also about 7% of the nitrogen is converted into other compounds, and so escapes gas volumetric estimation. For many clinical purposes, however, relative values are sufficient. An apparatus is described which permits in three flasks the rapid consecutive performance of two parallel experiments, and a test with a known weight of urea. A U-shaped capillary gas burette is attached which permits the gas to be measured under atmospheric pressure. H. W.

The Catalytic Decomposition of an Alkaline Solution of Sodium Hypobromite by Copper Sulphate. Antagonistic Action of Iodine. P. Fleury (*Compt. rend.*, 1920, **171**, 957—960; *J. Pharm. Chim.*, 1920, [vii], **22**, 449—462).—The presence of copper as copper sulphate causes a steady decomposition of an alkaline solution of sodium hypobromite, thus interfering with the estimation of carbamide by this reagent. The decomposition increases rapidly with the concentration of the copper salt. Thus the presence of 1 part of copper as copper sulphate in 100,000 causes the decomposition of 42% of the hypobromite in twenty-four hours at 36—37°. The presence of 1 part in 1000 of potassium iodide or iodate completely inhibits this catalytic decomposition of the hypobromite solution. W. G.

Urea and Nitrous Acid. H. Doublet and L. Lescoeur (*Compt. rend. Soc. Biol.*, 1920, **83**, 1103—1105; from *Chem. Zentr.*, 1920, iv, 520).—The authors employ the following reaction, $CO(NH_2)+2HNO_2=4N+CO_2+3H_2O$, for the estimation of urea in urine. Sodium nitrite, 69 grams to the litre, and normal nitric acid are employed. Just before use, 20 c.c. of each of the solutions are mixed. This is sufficient to decompose 600 mg. of urea. The evolved carbon dioxide is received in a special apparatus containing sodium carbonate, and the precipitated calcium carbonate is estimated titrimetrically. S. S. Z.

Estimation of the Azotæmic Index. M. Laudat (*Compt. rend. Soc. Biol.*, 1920, **83**, 1023—1025; from *Chem. Zentr.*, 1920, iv, 519).—A description of experiments in which pure urea and xanthylurea (m. p. 260—261°) were used in the control estimations of urea and total nitrogen. S. S. Z.

Method for the Estimation of Urea by Soja-bean. E. L. Kennaway (*Brit. J. Expt. Path.*, 1920, **1**, 135—141).—A technique for the estimation of urea is described by which 1 mg. can be estimated with an accuracy of 97%. The ammonia produced is not removed by an air current, and is titrated by means of a comparator. In the case of serum, an alcoholic extract is used without evaporation. Chemical Abstracts.

Microchemical Reaction of Morphine. Koller (*Zeitsch. Allg. Vest. Apothverein*, 1918, 332; from *J. Pharm. Chim.*, 1920, [vii], **22**, 442—443).—Characteristic crystals are obtained when a drop of dilute morphine solution is treated with a drop of slightly acidified Mayer's reagent. W. P. S.

Reaction of Sparteine. E. H. Grant (*J. Amer. Pharm. Assoc.*, 1920, **9**, 704; from *J. Pharm. Chim.*, 1920, [vii], **22**, 441—442).—An aqueous solution of the alkaloid is rendered ammoniacal and extracted with chloroform; the chloroform solution is shaken with dilute sulphuric acid, the alkaloid again extracted with chloroform after the acid solution has been rendered ammoniacal, and the chloroform solution is evaporated. The residue is treated with bromine solution, evaporated to dryness, and the residue brought into contact with ammonia gas; a bright red coloration is obtained with as little as 0·0005 gram of sparteine. The residue must be removed from the source of heat immediately after the last trace of bromine solution has evaporated.
W. P. S.

Colorimetric Investigation of Tryptophan. II. Systematic Investigation of the Colorimetric Estimation of Tryptophan based on Voisinet's Reaction. The Application of this Method to Proteins and Organs. Otto Fürth and Fritz Lieben (*Biochem. Zeitsch.*, 1920, **109**, 124—152).—A suitable way of carrying out the estimation is as follows. To 2 c.c. of the solution a drop of 2% formaldehyde solution and about 15 c.c. of very concentrated hydrochloric acid are added; after about ten minutes, 10—12 drops of 0·05% sodium nitrite are also added, and the mixture made up to 20 c.c. with concentrated hydrochloric acid. After a short time, the violet coloration which is produced is compared with a standard tryptophan solution (0·1%). An error of about 10% was observed with this method. The estimation can also be carried out on insoluble and coagulated proteins without hydrolysis. The tryptophan content of a great number of proteins has been determined. S. S. Z.

Estimation of the Products of Degradation of the Protein Substances in Blood Serum. A. Bach and B. Sbarsky (*Compt. rend.*, 1920, **171**, 1175—1177. Compare A., 1916, i, 353, 682).—It has previously been shown that the reduction of nitrates by animal tissues is due to the combined action of a ferment and a co-ferment. Fresh milk contains the ferment, but not the co-ferment, but the latter is constituted by the products of degradation of proteins. For the estimation, 1 c.c. of serum, 0·2 gram of sodium nitrate, and 2 c.c. of fresh milk are incubated at 60° for half-an-hour. The liquid is then clarified by means of lead acetate, and in the filtrate the nitrite formed is estimated by the Hosvay-Lunge method.

The method has been applied to seven horses in the course of immunisation, and in every case it was found that the products of

degradation of proteins appeared in the serum on the day following the injection of the toxins, and then disappeared more or less rapidly. W. G.

The Estimation of Phosphatides. D. H. Brauns and John A. MacLaughlin (*J. Amer. Chem. Soc.*, 1920, **42**, 2238—2250).—The phosphatides are extracted from the material, previously dried, if necessary, with anhydrous sodium and calcium sulphates (compare Robertson, A., 1916, i, 350), with alcohol at 50—60°. The alcoholic extracts are evaporated to dryness and extracted with anhydrous ether. The ethereal extract is evaporated to 30—40 c.c. and extracted with a saturated solution of sodium chloride, the ethereal layer being separated, the ether removed, and the residue dried and weighed. In this material the phosphorus is estimated colorimetrically, as described by van Eck (A., 1918, ii, 370). As a check, another portion of the extracted phosphatide may be hydrolysed by acid, and in the product the choline may be estimated as its platinichloride and the amino-nitrogen by Van Slyke's method. W. G.

Maltase. II. Estimation of Maltase in Yeast. Richard Willstätter and Werner Steibelt (*Zeitsch. physiol. Chem.*, 1920, **111**, 157—179).—The fresh yeast is triturated with ethyl acetate until it liquefies, water is added, and the mixture is neutralised with ammonia. This yeast suspension is then made up to a definite volume with a known maltose solution and a buffer mixture; aliquot portions are withdrawn at two different intervals, the degree of hydrolysis estimated, and the "time value" calculated. The few experiments carried out by this method show that the most part of the maltase of the yeast is extracted in this way. This method is also suitable for the comparison of the hydrolyses of sucrose and maltose by a given yeast. S. S. Z.

A Test for Anti-Beri-beri Vitamin and its Practical Application. Casimir Funk and Harry E. Dubin (*J. Biol. Chem.*, 1920, **44**, 487—498).—A yeast suspension is prepared by shaking a loopful of a forty-eight hours' pure culture of yeast in 100 c.c. of Nägeli solution on a shaking machine for three hours. Measured quantities of this suspension are then incubated for twenty hours at 30° in the presence of the unknown vitamin solution, control tubes with a vitamin solution of measured strength being employed. After incubation, the fermentation is stopped by heating the contents of the tubes at 75° for a few minutes, and the amount of yeast is estimated by centrifugalising in a specially calibrated tube. By this means, the authors believe they have obtained a valuable test for the presence of the vitamin-*B*, although the presence of inhibiting substances may interfere with the reaction in some cases. A number of substances were tested for the presence of the vitamin-*B* by this method. J. C. D.

General and Physical Chemistry.

Effects of Ring Closure on Spectrochemical Properties. II. Unsaturated Heterocyclic Compounds. K. VON AUWERS (*Annalen*, 1921, **422**, 133—159. Compare A., 1918, ii, 343).—The relations between unsaturated heterocyclic substances and the corresponding open-chain compounds are very involved; influences, the nature of which is still not fully understood, operate to mask regularities which undoubtedly exist. The author therefore refrains from dealing with the spectrochemistry of heterocyclic compounds in general, in the knowledge of which too many gaps still exist, and limits himself to a comparison of oxygen-containing heterocyclic compounds with corresponding unsaturated open-chain compounds, for example, α-pyrone and the ketone,

$$CHMe{:}CH{\cdot}CH{:}CH{\cdot}COMe,$$

2 : 6-dimethyl-γ-pyrone and phorone, coumarones and chromens and *o*-alkyloxystyrenes. The results show that there is as little fundamental difference between unsaturated *iso*- and hetero-cyclic compounds as between the corresponding saturated substances (*loc. cit.*). The production of a heterocyclic structure from an unsaturated open-chain compound causes, as a rule, a weakening of the exaltation, and, as in the case of saturated substances, the more so the more unsaturated is the chain. Alkyl or other substituents produce an effect opposed to that of ring closure.

The following substances are new: 1 : 2 : 4-*trimethylcoumarone*, $C_6H_3Me{<}{}^{CMe}_{-O-}{>}CMe$, colourless, highly refractive oil, b. p. 109·5—111°/10 mm., obtained in the usual manner from 1 : 4-dimethylcoumaranone and magnesium methyl iodide (2 mols.) in ethereal solution, has $D_4^{14\cdot0}$ 1·0267, D_4^{20} 1·021, n_α 1·54685, n_D 1·55332, n_β 1·56865, n_γ 1·58330 at 14·0°, n_D^{20} 1·5506; 1 : 4-*dimethyl*-2-*ethylcoumarone*, b. p. 124·7—124·8°/14 mm., has $D_4^{11\cdot4}$ 1·0108, D_4^{20} 1·003, n^α 1·54187, n_D 1·54715, n_β 1·56233, n_γ 1·57583 at 11·4°, n_D^{20} 1·5433.

C. S.

List of the most Sensitive Rays of the Elements, suitable for use in their Detection. A. DE GRAMONT (*Compt. rend.*, 1920, **171**, 1106—1109).—The author has tabulated the most sensitive rays for eighty-three of the elements obtained in the condensed spark, with or without self-induction. The ultimate rays are indicated. The rays are tabulated as (*a*) observed by the eye, (*b*) observed by photography either with a crown uviol spectrograph or a quartz spectrograph.

W. G.

Molecular Phase Hypothesis, a Theory of Chemical Reactivity. E. C. C. BALY (*Engineering*, 1919, **108**, 574—575).—The new views advanced are an outcome of studies on light absorption, especially in the infra-red. Ordinarily, curves of absorptive power (plotted against frequency) rise to rounded-off

peaks, but when the substances are cooled in liquid air or hydrogen, the curves narrow down and are seen to consist of a series of secondary peaks culminating in the line of maximal absorptive power. This line marks the characteristic frequency, and there are constant frequency differences between the secondary peaks of a group. The frequencies of the bands or lines so resolved represent multiples of some fundamental frequency in the infra-red, and each element has one or several characteristic frequencies. When two elements combine, the characteristic frequency of the compound is the least common multiple of the frequencies of the constituents. This can be accounted for on the quantum theory. Energy is lost by the combination of A and B, and if A has the characteristic frequency 5, B the frequency 7, then the emission of energy (and also its absorption) will occur in energy quanta of $5 \times 7 = 35h$ (where h is Planck's constant). To understand the mechanism, the simple atom may be regarded as something resembling a Saturn system, a nucleus surrounded by a ring of electrons, the whole representing a field of magnetic force, the lines of force passing through the ring. In groups of atoms, the fields may be symmetrical or not; similar or opposite poles will face one another, and the resulting field of force may hence be closed or open; the lines of force may be imagined to be closed (on themselves) even in a single atom. The fields are opened up by chemical activation. Reactivity now depends on the disposition of the field; the closed system will not display reactivity, and the molecules of a system may be in different phases, which will account for the varieties of modifications in complex molecules, for example, of sulphur. Valency is a measure of the number of characteristic frequencies. The group properties of the alkali metals, catalytic action, and ionisation are referred to from the point of view of this theory. CHEMICAL ABSTRACTS.

Ultra-violet Absorption Spectrum of Benzene Vapour. KARL SCHULZ (*Zeitsch. wiss. Photochem.*, 1920, **20**, 1—35).—The ultra-violet absorption spectrum of benzene vapour has been measured, using a concave grating, 6·47 metres radius of curvature and ruled with 15,450 lines per inch. The iron arc was used as source of light, and the first-order spectrum was photographed. Seventy-five bands were measured with an accuracy of 0·01—0·1 Å.U. The values are tabulated and compared with those of Witte (A., 1915, ii, 500). The structure of the spectrum is considered, and it is shown that a difference of 92·1 exists between the members of the long series. J. F. S.

Inorganic Luminescence Phenomena. II. Luminescent Boron Nitride. (Balmain's Aethogen) and the Excitation of Luminescence by Flames. ERICH TIEDE and FRIEDRICH BÜSCHER (*Ber.*, 1920, **53**, [*B*], 2206—2214. Compare A., 1920, ii, 723).—Balmain discovered boron nitride in 1842, and reported that it glows with a green light when held in the edge of a flame, but, like Wöhler (1850), he ascribed the phenomenon to a slow

oxidation of the substance. Various preparations of boron nitride have now been obtained, and it is found that unless they contain free boric acid, they do not exhibit the phenomenon. The effect is best produced by heating with a hydrogen flame, but is quite as strong in a flame obtained by burning chlorine in hydrogen. The luminescence is therefore not due to oxidation, but is physical in origin. As far as can be proved by chemical means, no foreign metallic impurity is necessary, but inactive samples can be rendered thermoluminescent by fusing them with boric acid in a well-closed crucible. The colour of the light emitted changes from blue to pale green with rise of boric acid content, but when there is more than about 10% of boric acid present, the effect is no longer observed.

All the thermoluminescent specimens are also phosphorescent, the effect being observed after exposure to daylight, an arc light, mercury-vapour light, *X*-rays, radium rays, and especially cathode rays. Moreover, specimens which emit green light when heated give green light after exposure to cathode rays, and blue thermoluminescence is paralleled by blue phosphorescence. What is more, specimens which contain too much boric acid to respond to the heat effect, such as those which have been heated in the air, and so allowed to oxidise, are nevertheless strongly phosphorescent with sky-blue to cyan-blue light. If such specimens, however, are heated sufficiently to melt the encrusting boric acid, the core suddenly exhibits its thermoluminescence. It appears that the small amount of boric acid necessary to cause the heat effect is intimately combined with the boron nitride.

Other thermoluminescent substances are lime containing a trace of bismuth or manganese (Donau, A., 1913, ii, 743; Paneth, A., 1919, ii, 67, 68), and phosphorescent zinc sulphide and silicate. In the case of zinc sulphide, the light emitted after exposure to daylight is yellow, but after heating with a hydrogen flame, green. The flame seems to be necessary to activate the preparation, for a specimen needs merely to be touched by the flame in order to make it glow subsequently on an electric hot-plate. Boron nitride placed in a carbon boat heated to redness by an electric current also glows so strongly where the carbon monoxide flame touches it that the blue light overshadows the red. What it is about the flame, whether ultra-violet radiations or emission of ions or electrons, that causes this activation is briefly discussed, but without any definite conclusions being reached. J. C. W.

Inorganic Luminescence Phenomena. III. Phosphorescence of Boric Acid. ERICH TIEDE (*Ber.*, 1920, **53**, [*B*], 2214—2216).—If boric acid is dehydrated either in the air or in a vacuum over phosphoric oxide, either slowly at 300° or quickly at red heat, it becomes phosphorescent, the phenomenon reaching a maximum with a certain, minute proportion of water still present, but disappearing as full dehydration is attained. The exceptionally bright light emitted does not continue for long, and

may be excited by an arc or mercury lamp, but not by cathode, X-, or radium rays, or by heat. J. C. W.

Photochemical Studies. XI. Photochemical Equilibria. JOH. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1920, **20**, 93—122. Compare A., 1920, ii, 461).—A theoretical paper in which the theoretical considerations in connexion with the equilibria in photochemical processes are treated mathematically. J. F. S.

Photochemistry of Alkyl Iodides and Iodine Solutions. HANS STOBBE and PAUL SCHMITT (*Zeitsch. wiss. Photochem.*, 1920, **20**, 57—92).—Alkyl iodides, either pure or in solution in paraffins, light petroleum, benzene, toluene, chloroform, ethyl ether, carbon tetrachloride, phenetole, acetic esters, or nitrobenzene, do not become coloured when preserved in the dark for two and a-half months. But in daylight a coloration is produced in a few hours in all cases. The coloration does not occur if oxygen is absent. The action of ultra-violet light on solutions of ethyl iodide, in benzene or carbon tetrachloride at 46—48°, and also in ethyl alcohol, has been studied. Solutions (6·25*N*) of methyl iodide, *n*-propyl iodide, and *iso*propyl iodide in benzene and ethyl alcohol have also been studied. It was also found that a solution of iodine in benzene or chloroform, after illumination for twenty hours with a quartz mercury lamp, on dilution gave a yellow solution, and not a red solution, as untreated iodine solutions do. To explain this action, the absorption spectrum of iodine, in alcohol, aqueous alcohol, methyl alcohol, propyl alcohol, *iso*propyl alcohol, and *sec*.-butyl alcohol solutions has been measured. Measurements were also made with alcoholic solutions of iodine to which organic iodides, ether, anisole, phenetole, and dimethylpyrone had been added. The experiments show that the decomposition of alkyl iodides with the liberation of iodine is an oxidation. Ethyl, methyl, and *n*-propyl iodides are similar in their behaviour toward light, but *iso*propyl iodide is much less stable. Iodobenzene behaves similarly to the primary aliphatic iodides. Ethyl bromide is decomposed by ultra-violet light of short wave-length with the liberation of bromine. Solutions of iodine in alcohols pass, in the course of time, into solutions of periodides (hydrogen tri-iodide or other additive compounds); this reaction is accelerated by light or spongy platinum. The absorption spectrum of true solutions of iodine consists of a single absorption band in the visible part of the spectrum, the position of which is independent of the nature of the solvent. The more the absorption is displaced toward the violet end of the spectrum the greater is the heat of solution of iodine in the solvent. When such solutions are diluted with several volumes of benzene or chloroform, the colour immediately becomes red. The spectrum of the periodide solutions shows two absorption bands in the ultra-violet with frequencies 2800 and 3450, and on dilution with benzene or chloroform yellow solutions are obtained. During the change of iodine into the periodide, solutions of mixtures are formed which show three absorp-

tion bands. The spectra of iodine described by various observers indicate that from 5% to 100% of the iodine present had been converted into periodide. Dimethylpyrone iodide exhibits the same spectrum as the periodide. J. F. S.

Beta ray Emission from Thin Films of the Elements exposed to Röntgen Rays. Lewis Simons (*Phil. Mag.*, 1921, [vi], **41**, 120—140).—Thin films of arsenic, selenium, zirconium, silver, tin, antimony, barium, gold, lead, and bismuth have been exposed to *X*-rays from a Coolidge tube with barium or silver secondary radiators and the radiation examined. It is shown that it is improbable that the maximum speed of ejection of electrons from different substances under the influence of *X*-rays of definite wavelength is exactly constant, independently of the nature of the substance, and dependent only on the frequency of the incident *X*-rays. The present experiments show that throughout the whole range of motion the distribution of electrons depends fundamentally on the substance from which they are emitted, but the difference, if any, in the maximum velocities is too small to be demonstrable by this method. The experimental results point to the conclusion that there may be speeds of emission of electrons from an atom *S* when *X*-rays of frequency v fall upon it, given by either $\frac{1}{2}mv^2 = hv - {}_S(hv_K + hv_L + hv_M + \ldots)$, each successive speed being given by the removal of a term from the bracket, commencing with the term $\frac{1}{2}mv^2 = hv - {}_S(hv)_{K \text{ or } L \text{ or } M}$, or the expression in brackets representing the potential energy of the electron from whichever atomic ring it was ejected, v_K, v_L, etc., being the *K*, *L*, etc., frequencies of the *X*-ray spectral lines of the parent atom, *S*. The experimental data agree rather better with the latter expression. There is a type of electronic emission fundamentally associated with each type of *X*-ray emission. Assuming that it is not a necessary condition that each of the radiating atoms of one substance should be emitting all possible types of spectral lines, from those of the highest energy downwards, then the energy of electronic emission of any one of these atoms is complementary to that of its wave-emission; in other words, the "*K*" electron is the slowest on emergence, the concomitant "*L*" electron faster, and so on. J. F. S.

Radiating Potentials of Nitrogen. H. D. Smith (*Physical Rev.*, 1919, **14**, 409—426).—A formula is derived for the distribution of the velocities of the impact electrons which may be applied to the observed values for the radiating potentials. Measurements gave (*a*) a strongly marked value at 8·294±0·04 volts, (*b*) a doubtful one at 7·3 volts, and (*c*) at low pressures a strong one at 6·29 volts. These values correspond with (*a*) $\lambda = 1490{\cdot}7$, a doublet noted by Lyman; (*b*) $\lambda = 1700$, the nearest known line is a doublet at 1744, which is sometimes also attributed to silicon; (*c*) $\lambda = 1965$, similar to a band at 1870. Traces of nitric oxide may have affected the values a little. From (*a*) the upper limit of the heat of dissociation of the nitrogen molecule into atoms is 190,000 cal., and from (*b*)

the most probable value is 145,000 cal. Qualitative evidence is given supporting the ionising potential for nitrogen at 18 volts as obtained by Davis and Goucher. CHEMICAL ABSTRACTS.

The Question of the Existence of Isotopes with the same Atomic Weight. STEFAN MEYER (*Zeitsch. physikal. Chem.*, 1920, **95**, 407—433).—See A., 1919, ii, 384.

Dielectric Constant of Selenium Oxychloride. JAMES E. WILDISH (*J. Amer. Chem. Soc.*, 1920, **42**, 2607—2609).—The dielectric constant of selenium oxychloride (b. p. 179·4° at 745·44 mm.) has been determined at 0°, 10°, and 20° by the Schmidt modification of Drude's method. As a mean of experiments with three cells, liquid selenium oxychloride has a dielectric constant at 20°, $46·2 \pm 1$, and at 10°, $51·00 \pm 0·5$; solid selenium oxychloride has the constant $16·8 \pm 2$ at 0°. The dielectric constant has a temperature-coefficient of 1·04%. J. F. S.

The Variations with Temperature of the [Electrical] Conductivity of Calcium Sulphide. P. VAILLANT (*Compt. rend.*, 1920, **171**, 1380—1383).—When a thin layer of calcium sulphide, previously insulated, is heated its conductivity increases rapidly, the curve showing a very acute maximum, and then decreases practically to zero. The gradient conductivity-temperature is greater and the maximum higher when the heating is more rapid. This phenomenon is connected with the state of phosphorescence, as, if the specimen is allowed to cool before the conductivity has become zero and is then heated again, much smaller variations and maxima are obtained. The increase in temperature has two effects on the conductivity of the calcium sulphide, varying its instantaneous value and increasing the amount of variation with duration of heating. The first effect, where duration of heating does not intervene, is governed by the equation $c = 1·17e^{0·130T}$, where T is the temperature, and c is the conductivity. The variation of c with the time at different temperatures is, for each temperature observed, an exponential variation of the type $c = c_0e^{-bt}$, the coefficient b being itself a linear function of the temperature. W. G.

Conductivity Cell. FRANK E. RICE (*J. Ind. Eng. Chem.*, 1920, **12**, 1202).—A cell for use in measuring the conductivity of solutions consists of a glass tube about the size of an ordinary burette; two platinum wires are fused through the sides of the tube at some distance apart, and platinum bands are fitted round the tube and over the outer ends of the wires. The wires inside the tube are sufficiently long to reach to one end and outside the tube, and one inside tube is covered with narrow glass tubing for the purpose of insulation. The ends of the tube are closed with rubber stoppers and a thermometer passes through the stoppers and tube, the bulb of the thermometer extending just through one stopper, so that it

comes into contact with the liquid in which the tube is immersed during a test. W. P. S.

Ionisation of Aqueous Solutions of Ammonia in the Presence of Carbamide. WINTHROP M. BURKE (*J. Amer. Chem. Soc.*, 1920, **42**, 2500—2506).—The equivalent conductivity of ammonia at various concentrations in $2M$-carbamide solution has been determined at $25{\cdot}00^\circ \pm 0{\cdot}01^\circ$ with the object of ascertaining whether the ionisation in this solvent, which has a greater dielectric constant than water, is greater than in pure water, as from analogy should be the case. The results show that the ionisation of ammonia in carbamide solution, as in pure aqueous solution, conforms with the law of mass action, but the ionisation constant is $12{\cdot}92 \times 10^{-6}$ in carbamide solution as against $18{\cdot}1 \times 10^{-6}$ in aqueous solution, thus presenting an exception to the Nernst-Thomson hypothesis. This difference (30%) cannot be due entirely, or to any large extent, to a change in viscosity, and it is possible that an ammonium–carbamide complex is formed which has a smaller ionisation constant than ammonium hydroxide. J. F. S.

Conductivity and Viscosity of Solutions in Dimethylamine, Trimethylamine, Ethylamine, Diethylamine, Triethylamine, and Propylamine. HOWARD MCKEE ELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 2454—2476).—The electrical conductivity and the viscosity of solutions of various concentrations of silver nitrate, silver iodide, barium thiocyanate, lithium chloride, ethylamine hydrochloride, and dimethylamine hydrochloride in the solvents named in the title have been determined at $-33{\cdot}5^\circ$. It is shown that dimethylamine is a poorer solvent than ethylamine, although the salts which did dissolve formed solutions which have about the same molecular conductivity. Diethylamine is a still poorer solvent and a distinctly poorer ionising solvent, a solution of lithium chloride in this solvent being no better a conductor than silver iodide in ethylamine. The tertiary amines are not good electrolytic solvents, no evidence of salt solution being found in any case, and the solvent in equilibrium with the solid solute did not gain appreciably in conductivity. The aminolysis of barium thiocyanate in solution in ethylamine has been followed by conductivity measurements for ninety-five hours. The specific conductivities of some of the solvents at $-33{\cdot}5^\circ$ are recorded: trimethylamine, $2{\cdot}2 \times 10^{-10}$; ethylamine, $4{\cdot}6 \times 10^{-8}$; and diethylamine, $2{\cdot}2 \times 10^{-9}$. The viscosities measured are: ammonia, $2{\cdot}54 \times 10^{-3}$; ethylamine, $5{\cdot}749 \times 10^{-3}$; dimethylamine, $4{\cdot}368 \times 10^{-3}$; trimethylamine, $3{\cdot}208 \times 10^{-3}$; diethylamine, $8{\cdot}236 \times 10^{-3}$; and triethylamine, $7{\cdot}726 \times 10^{-3}$, all at $-33{\cdot}5^\circ$. The following densities at $-33{\cdot}5^\circ$ are also given: dimethylamine, 0·727; trimethylamine, 0·702; ethylamine, 0·742; diethylamine, 0·713; and triethylamine, 0·778. J. F. S.

Saturated Potassium Chloride Calomel Cell. HAROLD A. FALES and WILLIAM A. MUDGE (*J. Amer. Chem. Soc.*, 1920, **42**, 2434—2453).—The *E.M.F.* of the combination

$$\mathrm{Hg,HgCl}\,|\,\mathrm{KCl(sat.)}\,||\,\mathrm{KCl(sat.)}\,|\,0{\cdot}1N\text{-}\mathrm{HCl}\,|\,\mathrm{H_2(Pt)}$$

has been measured over the temperature range 5—60° at intervals of 5°. Taking the value of the normal calomel cell at 25° as 0·5648 volt, the value of the saturated potassium chloride calomel cell at 25° is 0·5266 volt. It has a temperature-coefficient of +0·00020 volt/degree over the range 5—60°. The *E.M.F.* of the system Hg,HgCl | x*N*-KCl‖(sat.)KCl‖0·1*N*-HCl | H_2(Pt), and the value of the electrode, Hg,HgCl | x*N*-KCl, in the above system at 25° have been calculated for values of x ranging from 0·1*N* to 4·12*N*. The *E.M.F.* of the combinations

Hg,HgCl | 0·1*N*-KCl‖(sat.)KCl‖KCl(sat.) | HgCl,Hg,
Hg,HgCl | 1·0*N*-KCl‖KCl(sat.)‖KCl(sat.) | HgCl,Hg,
Hg,HgCl | 0·1*N*-KCl‖(sat.)KCl‖1·0*N*-KCl | HgCl,Hg,
Hg,HgCl | 0·1*N*-KCl‖KCl(sat.)‖0·1*N*-HCl | H_2(Pt),

and Hg,HgCl | 1·0*N*-KCl‖(sat.)KCl‖0·1*N*-HCl | H_2(Pt) has been measured over the temperature range 25—40° at intervals of 5°, and it is found that these combinations are quite untrustworthy above 25°, and only trustworthy at 25° for about one week. It is shown that the decrease in the *E.M.F.* of 0·1*N*- and *N*-potassium chloride calomel cells, when used in conjunction with a saturated salt bridge, is due to the diffusion of the concentrated solution of potassium chloride from the bridge into the cell, and not to the formation of a complex ion as a result of the interaction of the calomel and the potassium chloride solution. In preparing new calomel cells, it is necessary to use all new materials, and not simply replace the potassium chloride solution. The saturated potassium chloride calomel cell is the best cell for use in conjunction with a saturated salt bridge, because it has a very small temperature-coefficient, is easily reproducible, can be safely used at all temperatures from 5° to 60°, and can be relied on for its constancy of *E.M.F.* over long periods of time. J. F. S.

Recovery of Transmissivity in Passive Iron Wires as a Model of Recovery Processes in Irritable Living Systems. I. RALPH S. LILLIE (*J. Gen. Physiol.*, 1920, **3**, 107—128).—A paper in which certain processes occurring in the activation of passive iron wires are shown to be analogous to an irritable and conducting living element, such as a nerve fibre or muscle cell. When passive iron wire is dipped into nitric acid of a concentration above a certain critical concentration, the activation is only temporary, and is followed immediately by an automatic return of the metal to the passive condition. Activation initiated at any part of such a wire is thus transmitted rapidly along its whole length in a wave-like manner, each region as it becomes active activating the region adjoining, and immediately becoming passive again itself. In order to maintain activity in the living system, constant repetition of stimulation is necessary, and, similarly, chemical activity in a passive wire immersed in nitric acid (D 1·42) is an automatically self-limiting process, which can be maintained only by repeated contacts with the activating metal. After a wire

has been activated in the usual manner and has reverted to the passive state, it is found to be impossible to reactivate it until a definite interval of time has elapsed. This failure to reactivate the wire is comparable with the similarly inexcitable and non-conductive interval, or "refractory period," of irritable living systems. J. F. S.

The Crystallisation of Metals by Electrical Precipitation and certain Connected Phenomena. A. H. W. ATEN and (MLLE) LOUISE M. BOERLAGE (*Rec. trav. chim.*, 1920, **39**, 720—735).—The electrical precipitation of metals may result in any of the following, namely, (1) isolated crystals; (2) continuous layer with markedly crystalline structure; (3) perfectly supple, continuous layer without visible crystalline structure; (4) elongated, needle-like crystals; (5) a black deposit. The conditions governing, more particularly, the first type of deposit have been studied in the case of the electrolytic deposition of silver from a solution of silver nitrate. The forms are regulated by the three factors: number of crystals, velocity of growth of these crystals, variation of the polarisation tension with the current density. It is shown that the number of crystals per sq. mm. is practically a linear function of the intensity of the current, except when the current density becomes too great, and the number is greater the more dilute is the silver nitrate solution. It is only in the case where the polarisation tension is small that isolated crystals can be formed. A high value of $\Delta e/\Delta i$ will give a homogeneous, supple deposit. The formation of a uniform deposit of a metal on an irregular object is regulated by the magnitude of the variation of the polarisation tension with the current density. The addition of potassium nitrate, nitric acid, or gelatin to the solution of silver nitrate very considerably increases the number of crystals formed on a given area of the cathode. W. G.

Measurement of Low Magnetic Susceptibility by an Instrument of New Type. ERNEST WILSON (*Proc. Roy. Soc.*, 1921, **98**, [*A*], 274—284).—An instrument is described whereby the susceptibility may be measured over a wide range of magnetic force. The instrument, which makes no use of a scale and spot of light, is of a portable type. The force due to torsion in the Curie instrument is replaced by either an electromagnetic or an electrostatic system, in which the mechanical force is due to two components, one proportional to the magnetic force impressed on the specimen, and the other also proportional to the magnetic force in the case of constant susceptibility, but variable if the susceptibility varies. In the electromagnetic case, which is the method described, a moving coil is used, which is suspended in a magnetic field proportional in strength to the magnetic force acting on the specimen. It has the advantage that the absolute value of the susceptibility can be calculated from the known details of the instrument, and a considerable mechanical force can be produced. A full description of the construction and the theory of the apparatus is given, and

measurements are recorded for manganese sulphate, chrome alum, iron pyrites, kenyte, franklinite, green serpentine, grey granite, copper pyrites, and ferrous oxide. The following values of K_m, the mass susceptibility, are given for various values of H, the magnetic force: manganese sulphate, K_m $94 \cdot 2 \times 10^{-6}$ (mean), H 25—642 c.g.s.; iron pyrites, K_m $0 \cdot 99—0 \cdot 979 \times 10^{-6}$, H 168—740 c.g.s.; chrome alum, K_m $13 \cdot 7—13 \cdot 0 \times 10^{-6}$, H 49—717 c.g.s.; kenyte, K_m $253—300 \times 10^{-6}$ for H 26·5—134 c.g.s., with a maximum of 318×10^{-6} at 72·2 c.g.s.; copper pyrites, K_m 0·0102—0·0169, H 6·4—42·2 c.g.s.; and ferrous oxide, K_m 0·0128—0·0211, H 6·4—82·4 c.g.s.

J. F. S.

Magnetism and Atomic Structure. I. A. E. OXLEY (*Proc. Roy. Soc.*, 1921, **98**, [*A*], 264—274).—The close relationship which exists between the equilibrium positions of diamagnetic and paramagnetic crystalline substances suspended in a magnetic field, and the directions of the cleavage planes, can be satisfactorily interpreted in terms of a spacial distribution of electron orbits round the nucleus. The orbits may have any shape, but are probably small in comparison with atomic dimensions. In non-ionised media there is evidence that the coupling force between the units of the crystalline structure is that of magnetic induction, the mechanical stress accompanying it being balanced by the stress due to the distortion of the internal electrostatic configuration of the units. The coupling systems which account for these attractions are pairs of electron orbits. In this respect, the present theory is closely allied to the cubical atom theory of Lewis (A., 1916, ii, 310) and Langmuir (A., 1919, ii, 328), in which the most stable electron arrangement is that of a pair. Tyndall's discovery relating to the characteristic deportment of diamagnetic and paramagnetic substances in a magnetic field has been confirmed for a few organic compounds, and the interpretation of the results on the electron theory implies that, both in diamagnetic and paramagnetic crystals, the planes of the electron orbits have a greater aggregate projection perpendicular to the principal cleavage than parallel to it. Thus the existence of multiple cleavages demands a spacial distribution of electron orbits. Moreover, as the molecules are most closely packed in a direction parallel to the principal cleavage, the isolation of all the cleavages by suitably suspending the crystal in a magnetic field really isolates the unit of crystal structure. This unit is the chemical molecule. Crystals of the simple cubic form, for which X-ray analysis indicates an ionised atomic structure rather than a molecular structure, show no appreciable structural deportment in the magnetic field. It is probable that hydrogen and helium atoms when radiating are in a very different state from unexcited matter on which the magnetic observations have been made. In this work, the matter is in the normal state, and each atom contains at least one electron within the active range of another electron in an adjacent atom, and the mutual interaction of such systems must be taken into account. Some factor seems to

have been neglected in Bohr's hypothesis, which, though of little importance when the atoms contain only one electron each and are independent of each other, yet is of first importance for matter in the normal state, and without which it is impossible to explain either the magnetic properties of crystals or crystal structure. The attraction between exactly similar atoms, the directed valencies required by stereochemistry, and the directive forces within crystals are explicable only by a due recognition of the magnetic forcive in material media. It is probable that the Laplace intrinsic pressure in liquids and in isotropic gels is due to electrostatic doublets of atomic dimensions. When crystallisation occurs, superimposed on the electrostatic stresses are the directional stresses due to the magnetic doublets, which, for a given molecule, determine a characteristic crystalline symmetry, and, owing to their highly localised nature compared with the electrostatic doublets, determine the rigidity of the crystal. Such highly localised magnetic doublets suggest either that the conventional electron is moving in an orbit very small compared with atomic dimensions, or that the electron itself is a complex unit endowed with specific magnetic and electrostatic properties, that is, the electron is also a magneton.

J. F. S.

Critical Constants of Mercury and Increase of Molecular Attraction on Dissociation of Double Molecules. I. and II. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 267—281, 282—298. Compare A., 1918, ii, 8).—I. The critical temperature of mercury is estimated to be 1700°, the critical pressure at least 1100 atm., and the critical density about 4·15. At the critical point, mercury consists of Hg_2 and Hg. These conclusions are shown by calculation to be in accordance with other magnitudes. II. A mathematical consideration of the case of dissociation of double molecules from the point of view of thermodynamics and Van der Waals's equation. The results are applied to the case of mercury. J. R. P.

Critical Temperature and Pressure of some Substances. J. J. van Laar (*J. Chim. Phys.*, 1920, **18**, 273—282).—A theoretical paper in which methods of calculating the critical temperature and pressure from existing data are discussed and applied in a number of cases. The following values have been deduced and discussed in connexion with the existing experimental values: hydrogen fluoride, T_c 497·4°, p_c 99·6 atm.; hydrogen chloride, T_c 324·5°, p_c 81·7 atm.; hydrogen bromide, T_c 363·0°, p_c 74 atm.; and hydrogen iodide, T_c 423·5°, p_c 70 atm. J. F. S.

Some Relationships between the Absolute Values of the Critical Temperature and Boiling Point. Maurice Prud'homme (*J. Chim. Phys.*, 1920, **18**, 270—272).—The author has calculated the values of the constants of the three expressions $T_1/T_c=K_1$, $T_c/(T_c-T_1)=K_2$, $T_c/(T_c-T_1) \,.\, T_c/T_1=K_3$ for a number of elements and compounds. The two expressions

$(T_c - T_1) \cdot T_c/T_1 = \text{const.}$ and $T_1 \cdot (T_c - T_1)/T_c = \text{const.}$ are derived. These hold for homologous series; the former, for paraffins, chlorinated paraffins, olefines, ethers, aliphatic amines, and nitriles, and the latter for methylbenzenes, other substituted derivatives of benzene, esters, brominated paraffins, iodated paraffins, and phenols. It is also shown that between the three constants K_1, K_2, and K_3 the following relationship exists: $K_3 - K_2 = 1/K_1 = T_c/T_1$ or $K_1(K_3 - K_2) = 1$. J. F. S.

Relationship between the Absolute Values of the Critical Temperature, the Boiling Point, and the Melting Point. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1920, **18**, 307—310).—The author has applied similar relationships to those existing between the boiling point and the critical temperature to the freezing points. The expressions are $T_f/T_c = K_1'$, $T_c/(T_c - T_f) = K_2'$, and $T_c/(T_c - T_f) \cdot T_c/T_f = K_3'$ (see preceding abstract). It is shown that the expressions $T_c^2/T_1(T_c - T_1)$ and $T_c^2/T_f(T_c - T_f)$ are characteristic functions of both elements and compounds. They have not generally the same value, but the ratio between them is fairly constant for elements of the zero and seventh groups, and for many groups of analogous or homologous compounds. The expression $T_f(T_c - T_f) = rT_1(T_c - T_1)$ is stated to represent a general law, in which r is a constant having a value between 1·0 and 1·1. When $r = 1$, the expression becomes $T_c = T_f + T_1$, that is, the critical temperature is equal to the sum of the boiling point and the freezing point, all values being in absolute degrees. This is found to be the case for water, phosphine, methyl bromide, chlorobenzene, and acetone. Similar relationships are also found in the case of iron, copper, and gold, and in this case the above-mentioned empirical relationship is deduced theoretically. J. F. S.

Surface Energy, Latent Heat, and Compressibility. D. L. HAMMICK (*Phil. Mag.*, 1921, [vi], **41**, 21—32).—A theoretical paper in which expressions representing the surface energy, latent heat, and compressibility of liquids are deduced mathematically. The results obtained are tested by means of existing data, on ethyl ether, benzene, carbon tetrachloride, carbon disulphide, chloroform, ethyl acetate, ethylene dichloride, ethyl iodide, chlorobenzene, toluene, and nitrobenzene. It is shown that if the van der Waals's constant a is independent of volume, the compressibility, β, of a liquid should be connected with the internal latent heat by the expression $1/\beta J = -2\lambda_1 s$ (i), in which λ_1 is the internal latent heat and s the specific gravity. If a is a function of v, then $1/\beta J = \epsilon\lambda_1 s$ (ii), where $\epsilon = \rho/\alpha$ and $\rho = 1/\rho \cdot \partial\rho/\partial T$, that is, the coefficient of variation of surface energy with temperature, and $\alpha = 1/v\partial v/\partial T$, the coefficient of cubical expansion. It is found for the liquids examined that the expression (i) is approached at higher temperatures, the expression holding for some liquids at the boiling point, whilst (ii) becomes progressively applicable at low temperatures. Lewis's empirical approximation (*Zeitsch. physikal. Chem.*, 1911, **78**, 24),

that the heat of compression is very nearly equal to the latent heat of vaporisation per unit volume at 0°, is deduced. The approximate constancy of the product of the compressibility and surface energy at 0° is deduced, and the observed lack of constancy at other temperatures is explained. J. F. S.

The Melting Point of Heptane and the Law of Alternance of Melting Points. R. DE FORCRAND (*Compt. rend.*, 1921, **172**, 31—34).—A redetermination of the melting point of *n*-octane gives the value −57·4° (compare Guttmann, A., 1907, i, 458, who found −98·2°). A sample of heptane gave the values: b. p. 98·8°/760 mm.; m. p. −94·75°; D_4^0 0·7010. These values, taken in conjunction with the m. p.'s of the other members of the methane series of hydrocarbons, show that the m. p.'s of these hydrocarbons conform to the law of alternance from CH_4 to C_6H_{14}, and from C_7H_{16} to $C_{24}H_{50}$ they show a continuous rise, the rise always being greater from a hydrocarbon containing an odd number of carbon atoms to one containing an even number than vice versâ. The corresponding cyclic hydrocarbons from the C_3 to the C_8 member show the same alternance, and the author deduces for *cyclo*butane the approximate m. p., −50°. In the case of the silanes the m. p.'s show a continuous rise on ascending the series, but the rise is greater in passing from SiH_4 to Si_2H_6 or from Si_3H_8 to Si_4H_{10} than in passing from Si_2H_6 to Si_3H_8. W. G.

Distillation and Rectification. L. GAY (*Chim. et Ind.*, 1920, **4**, 735—748).—The author deals with the distillation of a mixture of three constituents and the continuous separation of these in different phases; methods and formulæ are given for calculating the composition of the different phases, and certain rules have been established concerning the minimum and maximum heat compatible with the correct operation of the fractionating and rectifying column. W. P. S.

Internal Energy of Inflammable Mixtures of Coal Gas and Air after Explosion. W. T. DAVID (*Proc. Roy. Soc.*, 1921, **98**, [*A*], 303—318).—In the first part of the paper the heat-loss measurements by conduction and by radiation made during the explosion and subsequent cooling of mixtures of coal gas and air of various compositions have been combined. The heat loss by conduction is 40—60% greater than the loss by radiation in the experimental vessel. In a vessel rather more than twice as large, the two losses would be equal, and in a still larger vessel the radiation loss would be the greater. Formulæ have been deduced whereby the total heat loss up to the moment of maximum pressure and the rate of heat loss at any temperature during cooling may be calculated from data obtained from the pressure–time curves. In the second part of the paper the heat-loss measurements have been applied to the estimation of the internal energy and the volumetric heat of the different mixtures at various temperatures after explosion. An

examination of the internal energy and volumetric heat curves so obtained indicates that at the moment of maximum pressure about 10% of the heat of combustion of the coal gas in each mixture has not been converted into thermal energy, and that after-burning continues for at least 0·25 sec. after the maximum pressure has been attained. These results show that the energy of combustion of the coal gas originally in the vessel is distributed at the moment of maximum temperature as follows: (1) Internal energy (thermal) from about 72% of the heat of combustion of the coal gas in a 9·7% mixture to about 80% in a 15% mixture. (ii) Available chemical energy, about 10% in each mixture. (iii) Heat loss to walls of vessel, from about 10% in a 15% mixture to about 18% in a 9·7% mixture. J. F. S.

A Determination, by means of a Differential Calorimeter, of the Heat produced during the Inversion of Sucrose. HENRY H. DIXON and NIGEL G. BALL (*Sci. Proc. R. Dubl. Soc.*, 1920, **16**, 153—164).—Using an apparatus similar in character to that of Hill (A., 1912, ii, 20), the differential calorimeter being formed by two vacuum flasks, the temperature measurements being made with a thermo-electric couple (compare Dixon, A., 1911, ii, 853), the authors have determined the heat of inversion of sucrose by invertase, and obtain the value 3·83 cal. per gram-molecule, which is in close agreement with the value obtained by Brown and Pickering (T., 1897, **71**, 783). Attempts to obtain a value for the heat of reaction during the hydrolysis of maltose were not successful. W. G.

The Fundamental Constants of Nature. HAWKSWORTH COLLINS (*Chem. News*, 1921, **122**, 2—4).—Evidence is brought forward to prove that the boiling points are not suitable temperatures for comparison of the molecular volumes of substances. J. R. P.

Viscosity-Concentration Function of Poly-disperse Systems. H. LÜERS and M. SCHNEIDER (*Kolloid Zeitsch.*, 1920, **27**, 273—277).—Viscosity measurements of mixtures of water and barley flour up to a concentration of 24 grams in 100 c.c. of solution have been made at 20°. It is shown that this case, as well as other complicated poly-disperse systems, are represented by the empirical equation $\eta_s=\eta_0(1+kf+k_1f^n)$, in which η_s is the viscosity of the suspension, η_0 that of water $(=1)$, f the volume relationship of the disperse phase to the total volume, k, k_1, and n are constants. This expression is similar to that put forward by Wo. Ostwald and Mündler for the osmotic pressure of dispersoids (A., 1919, ii, 185). The present system is also satisfactorily represented by the theoretically deduced formula $\eta_s=\eta(1-\alpha K)$ (Hess, this vol., ii, 18), in which η_s is the viscosity of the suspension, η that of the dispersion medium, K the quantity of disperse phase in unit volume of the suspension, and α a factor which converts K into the functioning volume of the disperse phase. J. F. S.

Surface Tension and Molecular Attraction. The Adhesional Work between Mercury and Organic Liquids. WILLIAM D. HARKINS and E. H. GRAFTON (*J. Amer. Chem. Soc.*, 1920, **42**, 2534—2538).—The surface tension of mercury in air, water, ethyl alcohol, ethyl ether, octyl alcohol, nitroethane, nitrobenzene, carbon disulphide, carbon tetrachloride, chloroform, methylene chloride, ethylidene chloride, ethylene dibromide, acetylene tetrabromide, methyl iodide, ethyl iodide, benzene, hexane, and octane has been determined at 20° by the method previously used by Harkins and Brown (A., 1919, ii, 221). From the results the adhesional work is calculated by means of the formula $W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$, in which W_A is the adhesional work, $-\Delta\gamma$ the decrease in free energy when the surfaces of the two liquids come together, γ_1 and γ_2 are the free surface energies per sq. cm. of the two liquids, and $\gamma_{1,2}$ is the free surface energy of the interface. The surface tension of mercury in air at 20° is 464·9 dynes, whilst in water the value is 374·8 dynes; the adhesional work in water is 182·6 ergs.

J. F. S.

Surface Energy of Mercury and the Energy Relations at the Interface between Mercury and other Liquids. WILLIAM D. HARKINS and WARREN W. EWING (*J. Amer. Chem. Soc.*, 1920, **42**, 2539—2547).—The surface tension of mercury in a vacuum has been determined at 0°, 10°, 20°, 30°, 40°, 50°, and 60° by the drop-weight method, and from the results the free energy of surface formation, the latent heat of surface formation, and the total energy of surface formation have been calculated. The entropy of surface formation is 0·22 ergs per degree per sq. cm. The interfacial tensions between mercury and a number of organic liquids have been determined at 20° by the drop-weight method. The results of the present work and the previous work (see preceding abstract) indicate that the adhesional work between a mercury surface and the surface of an organic liquid is always greater than that between the organic liquid and water, and also greater than that between the organic liquid and itself, that is, the cohesional surface work. In about half the cases examined the difference between the adhesional work against mercury and that against water is nearly constant, and lies between 80 and 90 ergs, so that the work of attraction is by no means entirely specific. The adhesional work decreases rapidly with increase of temperature, whilst the total adhesional energy increases. The latent heat of the interface between mercury and another liquid decreases rapidly as the temperature increases, whilst the latent heat of most ordinary surfaces increases with the temperature, and the total energy of interface formation also decreases, although not so rapidly. J. F. S.

Surface Tension of Oil-Water Interfaces. H. HARTRIDGE and R. A. PETERS (*Proc. Physiol. Soc.*, Oct. 16, 1920; *J. Physiol.*, **54**, xli).—The surface tension between olive oil and water depends greatly on the reaction of the water. Near the neutral point

there is a fall in the surface tension of about 35% for an increase of 1 in the P_H. It is hoped to base on this a means for determining the hydrogen-ion concentration of physiological fluids.

G. B.

The Surface Tension of certain Soap Solutions and their Emulsifying Power. MOLLIE G. WHITE and J. W. MARDEN (*J. Physical Chem.*, 1920, **24**, 618—629).—The surface tensions of solutions of sodium stearate and sodium palmitate were determined. Solutions of soap decrease in surface tension as they increase in concentration, whilst solutions of sodium hydroxide and many salts show the opposite behaviour. The relative emulsifying power of solutions of sodium palmitate and sodium stearate for petroleum and linseed oil was determined by shaking by hand for five minutes and observing the time of noticeable separation. With increase of concentration of the soap solution, there is an increase of emulsifying power, or, as the surface tension increases, the emulsifying power decreases. The viscosity has considerable influence on the permanency of the emulsions. The presence of glycerol does not affect the surface tension to any large extent, and should have no deleterious effect on the cleansing power of soap. A large amount of sodium carbonate, however, raises the surface tension, and would not be desirable in cleansing soaps.

J. R. P.

Absorption by Coagulation. F. DEZEINE (*J. Pharm. Belg.*, 1920, **2**, 238—240, 257—258, 281—282, 305—307, 329—332, 349—351, 389—390, 433—444).—Largely a theoretical discussion with a summary of the literature. The author has prepared dispersed copper sols by the Bredig method, and considers that the instances in which the disperse copper differs in chemical reaction from compact copper, as with acids and salt solutions in which copper ions or basic copper precipitates are formed without any evidence of a reducing action, may be explained by an action of the dissolved oxygen on the very extensive surface of the copper.

CHEMICAL ABSTRACTS.

Charcoal Activation. H. HORTON SHELDON (*Physical Rev.*, 1920, **16**, 165—172).—The first part of this paper comprises a study of the heat effect on the adsorption of hydrogen and nitrogen by charcoal, and is a continuation of the work of Lemon (A., 1920, ii, 167), in which air was used. The charcoal is heated for periods of one to twenty hours at 400—1000°, and, at the same time, the gases given off are pumped out with a mercury condensation pump. The activity of the charcoal is tested after each treatment by its adsorption of gas at liquid-air temperature, and the results are shown by curves, in which the logarithm of time in minutes is plotted against the logarithm of pressure in cm. The results obtained are in agreement with the hydrocarbon theory of activation proposed by Chaney. The second part of the work consisted

in the formation of a charcoal which adsorbed hydrogen more abundantly than nitrogen. This was done merely by heating at 1000° for about 3·5 hours in a vacuum maintained by continuous pumping with a mercury condensation pump. The apparent difference between the adsorption of hydrogen and of nitrogen is believed to be due to a secondary action in the first case, which is either a chemical action, or, as McBain believes, the formation of a solid solution. It is, however, reasonable to conclude that surface condensation is the principal action in the case of both gases.

CHEMICAL ABSTRACTS.

Adsorption by Precipitates. III. HARRY B. WEISER and EDMUND B. MIDDLETON (*J. Physical Chem.*, 1920, **24**, 630—663. See A., 1920, ii, 760).—The precipitation of colloidal alumina by electrolytes and the adsorption of the precipitating ions by the hydrous oxide were investigated. The results confirm those obtained with ferric oxide. The precipitating concentrations of a number of electrolytes for colloidal hydrous aluminium oxide were determined, and, on the assumption that the most readily adsorbed ion precipitates in the lowest concentration, and *vice versa*, the order of adsorption of anions deduced from the precipitation values, expressed in equivalents, is found to be: ferrocyanide, thiosulphate, ferricyanide, citrate, sulphate, oxalate, phosphate, chromate, dithionate, dichromate, chloride, nitrate, bromide, iodide.

The adsorption of multivalent ions, not readily removed by washing, was determined by direct analysis of the precipitate. The amounts of various anions carried down were not even approximately equivalent. Although the adsorption of equivalent amounts will neutralise a given amount of colloid, the actual amounts carried down will not be equivalent, since the amounts adsorbed by the neutralised particles vary with the adsorbability of the ions. The order of adsorption, beginning with the ion most adsorbed, is: phosphate, ferrocyanide, ferricyanide, oxalate, sulphate, chromate, thiosulphate, dithionate, dichromate. The order deduced from the precipitation values is not the same as that found by analysis, since the precipitation values are not determined exclusively by the valency and adsorbability of the ions.

The conversion of potassium dichromate into chromate in the presence of powdered alumina, noticed by Ishizaka (A., 1913, ii, 486), is explained by the disturbance of the equilibrium $Cr_2O_7'' + H_2O \rightleftharpoons 2H^{\cdot} + 2CrO_4'$ by the strong preferential adsorption of hydrion by the alumina. Colloidal alumina stabilised by preferential adsorption of hydrion has a comparatively slight effect on the equilibrium.

J. R. P.

Adsorption of Aniline Dyes and Inorganic Salts by Solutions of Lecithin. J. CRUICKSHANK (*J. Path. Bact.*, 1920, **23**, 230—232).—Ethyl ether alone did not remove dyes from aqueous solution. Solutions of lecithin in ether were very active in taking up dyes from aqueous solution. With suitable concentrations of

lecithin, practically all the dye could be removed. Very small amounts of lecithin exert this action; 0·00001 gram in 2 c.c. extracted a sufficient amount of brilliant-green and other dyes from 1% solutions to be detectable. Acid dyes were only slightly adsorbed. Various oils, fats, fatty acids, and soaps failed to exhibit this property, except that oleic and linoleic acids in large amounts produced slight coloration of the ethereal solutions. Cholesterol gave no evidence of adsorbent power. All results were the same when solutions were made in benzene or chloroform instead of ether. Potassium iodide, bromide, chromate, thiocyanate, ferro- and ferri-cyanide, sodium chloride, iodide, nitroprusside, arsenate, salicylate, and other salts were adsorbed from aqueous solution by ethereal solutions of lecithin. Quinine and strychnine were readily taken up, but codeine and morphine were not. Kephalin acted like lecithin. CHEMICAL ABSTRACTS.

Anomalous Osmosis with Gold Beaters' Skin Membranes. Chloride Solutions in the Presence of Acids and Bases. F. E. BARTELL and O. E. MADISON (*J. Physical Chem.*, 1920, **24**, 593—607).—The conclusions formerly arrived at (A., 1916, ii, 377, 388; 1920, ii, 595) have been confirmed by a study of the effects of different concentrations of acids and bases on the osmose of salt solutions. If the fundamental hypothesis is correct, it should be possible to change the osmotic effects of salt solutions by altering the sign of the charge on the membrane by addition of acids and bases. The same salts, apparatus, and methods were used as in previous experiments, and the expected results were found. The presence of acid or alkali may alter, not only the electrical sign of the capillary wall system, but also that of the membrane system. The direction of osmosis, and also its magnitude, are closely related to the electrical orientation of the cell system. The results are represented in tables and curves. J. R. P.

The Dissolution of Sodium Chloride and Sodium Chlorate Crystals. WALTER POPPE (*Jahrb. Min.*, 1914, *Beil. Bd.*, **38**, 363—428).—Experiments were made to test Johnsen's theory of the growth and dissolution of crystals, which is founded on the assumption that, under constant conditions, each crystal form has a constant velocity of growth or dissolution in a direction normal to the surface of the crystal face. The experiments were made by attaching the crystal to a horizontally revolving surface in a solution of the salt at 30°, undersaturated to a known extent (0·5% to 2·0%), and at stated intervals withdrawing the crystal and measuring its linear dimensions, and, when possible, the angles between the vicinal faces which developed. It was found that, with 0·5% and 1·0% undersaturated solutions, each crystal form dissolved with a specific constant velocity, but with 2% undersaturation the rates of dissolution of all faces became approximately equal, and the faces all became so rounded that it was impossible to measure the angles between them.

When a crystal of rock-salt, in the form of a cleavage cube, was placed in a 0·5% or 1% undersaturated solution, each cube face was replaced by four flat pyramid faces of the form $\{h10\}$, where h varied from 46 to 164. These faces, in turn, were gradually replaced by icositetrahedral faces having indices of the order $\{14.1.1\}$ to $\{23.1.1\}$. Experiments were also made in which the original crystal was a combination of cube and dodecahedron or octahedron. The dodecahedron had about the same solution velocity as the cube face, but that of the octahedron was much slower. Consequently, the octahedron faces quickly disappeared, since the final crystal faces are those which have the greatest solution velocity. The final crystal was an icositetrahedron.

Cubes of sodium chlorate in an undersaturated solution were transformed into a combination of two flat pentagondodecahedra, in agreement with the tetartohedral character of the crystal. In the course of the work, the solubility of sodium chlorate in water at 30° was redetermined, and found to be 104·6 grams per 100 grams of water, instead of 111·25 grams, as obtained from Landolt-Bernstein's tables. The saturated solution has D^{30} 1·450, and 100 c.c. contains 74·13±0·007 grams of sodium chlorate.

The results are discussed at some length, especially as regards their bearing on Noyes and Whitney's formula for the rate of solution of a solid (A., 1897, ii, 479). It cannot be concluded from the results that different faces of a crystal actually have different solubilities. If such different solubilities do exist, it is probably only when the particles are very small. E. H. R.

Nature of the Cleavage of Crystals. GEORG WULFF (*Physikal. Zeitsch.*, 1920, **21**, 718—720).—A theoretical paper in which the author makes the assumption that the cleavage of crystals occurs in planes of weak cohesion, due to a weak affinity. Thus, in the case of a binary compound AB of univalent elements, there are two methods in which an atom chain in a crystal may be arranged, $A—B—A—B—A—B$ . . . and

$$A—B—B—A—A—B\ .\ .\ .;$$

in the first arrangement there is no obvious position where cleavage might by preference take place, but in the second arrangement it is likely to occur between similar elements, in the positions $B—B$ or $A—A$, on account of decreased attractive force. The hypothesis is developed in the case of fluorspar, rock-salt, calcspar, zinc blende, diamond, and sulphur; diagrams representing the arrangement in these cases are given, and the cleavage planes deduced.

J. F. S.

The Existence of Equidistant Differentiated Planes Normal to the Optic Axis in Anisotropic Liquids (Liquid Crystals). F. GRANDJEAN (*Compt. rend.*, 1921, **172**, 71—74).—To explain the colours given by reflection by negative anisotropic liquids, authors have suggested a division of these liquids into parallel plates of constant thickness, at the surface of

which the light will be reflected. The author shows that such plates are distinctly visible under the microscope in the case of amyl cyanobenzylideneaminocinnamate. The liquid is examined in a cleavage crevice of some mineral, such as mica or talc, having a perfect cleavage. For this ester, the equidistances between the bands are $1{\cdot}88 \times 10^{-5}$ cm. at 92°, the m. p. of the solid crystals, and $2{\cdot}18 \times 10^{-5}$ cm. at 105°, the temperature of transformation into an isotropic liquid. W. G.

Swelling of Colloidal Mixtures. I. HANS HANDOVSKY and ARTHUR WEIL (*Kolloid Zeitsch.*, 1920, **27**, 306—311).—The maximum swelling of 20% gelatin jellies and the influence of charcoal and lipoid substances on the jellies have been examined. It is shown that the addition of animal charcoal in quantities up to 33% to 20% gelatin jellies has no effect on the swelling, and that charcoal and gelatin form complexes each with its own power of swelling. Similar conclusions are reached in the other mixtures examined. J. F. S.

Colloid Chemical Action of Salts of the Rare Earths and their Relationship to the Precipitation Reaction of the Anti-Substances. R. DOERR (*Kolloid Zeitsch.*, 1920, **27**, 277—292).—The behaviour of the salts of thorium, cerium, praseodymium, and lanthanum has been examined in connexion with a large number of colloidal substances, such as sera of a number of animals. The salts examined agglutinate suspensions of cells (red blood corpuscles, bacteria, and spores), and precipitate albumin sols. This happens when the salt is present as a typical crystalloid and also when the salts are not hydrolysed in the solution. Agglutination and precipitation take place with very small concentrations of salts (1 part of thorium sulphate to 5000—10,000 parts of the colloidal mixture). Quadrivalent cations (Th) act more strongly than tervalent cations (Ce, La, Pr); still, the precipitating power does not depend only on the valency, but also on other unknown properties of the cations of the rare earths and on the particular constitution of the albuminous substance. The salts examined are toxic toward both plant and animal protoplasm. The poisonous character is conditioned by the valency (Th more poisonous than Ce) of the cation, by the nature of the cation, and by the sensitiveness of the living cell. Different cells show very different powers of resistance; spirochætes are much more resistant than typhus baccilli. The mechanism of the poisoning is not due to the simple coagulation of the albumin, for in the presence of excess of albumin the coagulation is reversible, but the poisoning is not. Spores of bacteria and fungi are not attacked because of the impermeability of their membranes. The ease with which these substances agglutinate indicates that this process is a surface reaction. The coagulation of albumin by the salts of the rare earths is retarded by an excess of one of the reacting substances. For the maximum relationship at which coagulation will occur there is a minimum salt concentration, below

which no coagulation can take place. This concentration lies lower for the thorium cation than for cerium, praseodymium or lanthanum. The coagulation depends on the formation of loose compounds of albumin and salt (cerium albuminate), similar to those formed with the heavy metals. These compounds are colloid-chemically inactive and easily reversible; they dissolve readily in an excess of either component, and in this the different sorts of albumin, as well as the different cations, can replace one another. The dissolving power of the cations is proportional to the coagulating power. Thorium salts dissolve much better than cerium salts. The analysis of such precipitates by means of Löwe's interferometer shows that the quantity of substance coagulated does not depend only on the relative concentration, but also on the cation of the salt, and in the case of thorium is three times as great as that produced by twenty times the quantity of cerous chloride.

J. F. S.

Simple Method of Preparing Ultra-filters. ERICH KNAFFL-LENZ (*Kolloid Zeitsch.*, 1920, **27**, 315—316).—An ultra-filter for use with a Buchner funnel or a Gooch crucible may be prepared as follows: Into a crystallising dish of the same internal diameter as the Buchner funnel, or into a porcelain crucible of the same internal diameter as the Gooch crucible, a 3% solution of collodion is poured and equally distributed by rotation of the dish. As soon as the ether has evaporated, the dish is filled with water three or four times, and finally the membrane is removed by loosening it at the edges and allowing water to flow between it and the glass. It is then placed in the Buchner funnel, which contains a filter paper, and carefully pressed on to the sides and bottom. J. F. S.

Studies in Emulsions. II. The Reversal of Phases by Electrolytes, and the Effects of Free Fatty Acids and Alkalis on Emulsion Equilibrium. SHANTI SWARUPA BHATNAGAR (T., 1921, **119**, 61—68).

Double Saline Decompositions and the Law of Phases. ÉTIENNE RENGADE (*Compt. rend.*, 1921, **172**, 60—62. Compare A., 1917, ii, 451).—In a discussion of Raveau's work (this vol., ii, 31) the author considers the effect of the addition of a small amount of water to a mixture of sodium nitrate and ammonium chloride. From results obtained by adding crystals of sodium nitrate to a saturated solution of ammonium chloride, or by shaking an excess of sodium nitrate (0·588 mol.) and ammonium chloride (0·467 mol.) with a little water, it is shown that at the ordinary temperature there are only two ternary mixtures, namely,

$$NaNO_3\text{–}NH_4\cdot NO_3\text{–}NH_4Cl$$

and $NaNO_3$–NH_4Cl–$NaCl$, which can exist without change in contact with a small amount of water. All other mixtures of the two, three, or four salts, containing the four ions, decompose, giving, according to the conditions, one or other of the ternary mixtures.

In general, when any two salts with different ions, belonging to a "stable couple," are in contact with water, a third solid salt will appear or not, according as the concentration of this third salt in solution is superior or inferior to its actual solubility. W. G.

Corrosive Action of Chlorine-treated Water. I. The Effects of Steel on the Equilibrium: $Cl_2 + H_2O \rightleftharpoons HCl + HClO$, and of Products of the Equilibrium on Steel. GEORGE L. CLARK and R. B. ISELEY (*J. Ind. Eng. Chem.*, 1920, **12**, 1116—1122).—Rusting of steel occurs in water free from chlorine and is caused by the presence of dissolved oxygen. In the presence of chlorine, the most active agent is hypochlorous acid, which disappears first from the solution; rust is formed rapidly during the disappearance, and then practically ceases when the concentration of hydrochloric acid becomes constant. This indicates an equilibrium, $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. It has been shown that the reaction $H_2O + Cl_2 \rightleftharpoons HOCl + HCl$ proceeds very slowly and comes to equilibrium. In deciding whether iron actually acts as a catalyst in materially hastening the final attainment of equilibrium in this reaction, it is apparent that, in the presence of chloride, the iron is present almost completely in the form of ferric ion, and that the concentration of ferrous ion which can react with ClO^- is very small. The effect of iron is, therefore, practically entirely chemical rather than catalytic in nature. W. P. S.

The Fusion of Potassium Salts and Mixtures of Salts containing Water of Crystallisation. I. and II. E. JÄNECKE (*Kali*, 1916, **10**, 371—375; 1917, **11**, 10—13, 21—26; from *Jahrb. Min.*, 1920, i, *Ref.* 262—263, 263—265).—I. The separation of the melt and residue in the incongruent fusion of potassium salts and mixtures with other salts was effected in a special apparatus under pressure. A diminution of pressure was observed at the melting point. Gypsum, $CaSO_4,2H_2O$, exhibits incongruent fusion at 128—130°, the solution pressed out being very dilute and the residue having the composition $CaSO_4,\frac{1}{2}H_2O$. The hydrate, $MgSO_4,7H_2O$, is in equilibrium at 51° with a melt of given composition and the hydrate, $MgSO_4,6H_2O$, which may be separated by pressing. The hexahydrate shows an anomaly in its incongruent fusion, since the equilibrium at 68° between this salt, kieserite, and melt can readily be superheated. The pressed residue contains so much mother liquor as to lead to the suspicion of the formation of an intermediate hydrate. The displacement of the incongruent melting point by pressure is also possible.

II. The behaviour of other salt pairs in the pressure apparatus was studied, including the fusion of kainite, of a mixture of kainite and carnallite, and the transition of a mixture of reichardtite, sylvine, and carnallite into kainite and melt. The incongruent fusion of kainite occurs theoretically at 85°; in many cases 155—165° was reached under pressure; the transition temperature of kainite and carnallite may also be much above the theoretical value according to the conditions. By very slow heating the theoret-

ical values are found. In the formation of the Stassfurt deposits the melts formed by incongruent fusion may have been pressed out and thus the reverse changes prevented. The influence of pressure may also have been present. J. R. P.

Ternary Systems with Three Solid Phases of a Special Kind. The Systems (Ba–K–Na)Cl, Mg–Cd–Zn, and similar Cases. ERNST JÄNECKE (*Jahrb. Min.*, 1914, *Beil. Bd.*, **38**, 501—512).—The paper is devoted to a theoretical discussion of the equilibrium conditions in ternary systems, in which, of the three components, *A*, *B*, and *C*, *A* and *C* are completely miscible, another pair, *B* and *C*, form a binary eutectic, whilst the remaining pair, *A* and *B*, form a compound. The system $KCl–BaCl_2–NaCl$ is a typical example. Assuming that KCl and NaCl form a continuous series of mixed crystals in the ternary mixture, the only three solid phases which can appear when this ternary system crystallises are mixed crystals KCl + NaCl, the compound $BaCl_2,2KCl$, and $BaCl_2$. These three phases correspond with three areas in the triangular equilibrium diagram, separated from one another by three curves which meet in an invariant point *E*, which in this case is a eutectic point in equilibrium with the three phases, $BaCl_2$, $BaCl_2,2KCl$, and mixed crystals of sodium and potassium chlorides of a particular composition, called by the author the "principal mixed crystal." According to Gemsky, who investigated this system (A., 1914, ii, 51), potassium and sodium chlorides do not form a continuous series of mixed crystals in the ternary system, but two series, one rich in sodium and the other rich in potassium, with a gap between. This opinion is criticised by the author on the ground that it leads to results contradictory to the phase rule, since four phases appear in equilibrium at the invariant point *E*. Gemsky's results may be explained on the assumption that complete equilibrium between the solid and liquid does not obtain during crystallisation, with the result that mixed crystals of varying composition appear. The equilibrium diagram of the system Mg–Cd–Zn is discussed, and also similar theoretical cases in which the invariant point becomes a ternary transition point, instead of a eutectic point. E. H. R.

The System Barium Chloride–Potassium Chloride–Sodium Chloride. E. VORTISCH (*Jahrb. Min.*, 1914, *Beil. Bd.*, **38**, 513—524. Compare preceding abstract).—Further experiments have confirmed Gemsky's results (*loc. cit.*). The existence of two series of mixed crystals of sodium and potassium chlorides in the ternary mixture does not conflict with the phase rule. Shortly before the eutectic crystallisation a resorption of the mixed crystals rich in potassium chloride occurs, so that only three solid phases are in equilibrium at the invariant point. This conclusion was confirmed by microscopic examination of thin sections. E. H. R.

The System Barium Chloride–Potassium Chloride–Sodium Chloride. ERNST JÄNECKE (*Centr. Min.*, 1919, 271—274). —Polemical, in reply to Vortisch (preceding abstract). Mixed

crystals of potassium and sodium chlorides begin to separate in the solid state only below 375°, and since the eutectic temperature is 542°, it follows that no separation can take place before the eutectic crystallisation. It is demonstrated mathematically, with the help of the thermodynamic potential (*Z*-function), that the system under consideration conforms to the type of ternary system to which it was previously assigned by the author. E. H. R.

Mixed Crystals (K,Na)Cl in Ternary Systems. ERH. VORTISCH (*Centr. Min.*, 1919, 293—299); ERNST JÄNECKE (*ibid.*, 358).—Vortisch replies to Jänecke (preceding abstract). It is shown that in other ternary systems, in particular the system $CdCl_2$–KCl–NaCl, a gap occurs in the mixed crystal series NaCl–KCl. It has been shown by Nacken (A., 1919, ii, 281) that the limiting temperature of complete miscibility of potassium and sodium chlorides is probably 500°, not 375°. In presence of a third component this limiting temperature is probably raised considerably, and the gap in the mixed crystal series found by Gemsky in the ternary system $BaCl_2$–KCl–NaCl is thus accounted for.

To this, Jänecke replies briefly. E. H. R.

Thermal and Crystallographic Investigation of the Ternary Systems Lithium Chloride-Sodium Chloride-Potassium Chloride and Calcium Chloride-Strontium Chloride-Barium Chloride. WALTER SCHAEFER (*Jahrb. Min.*, 1919, *Beil. Bd.*, **43**, 132—189).—The melting points of the pure substances were redetermined: lithium chloride, 609°; sodium chloride, 802°; potassium chloride, 774°; calcium chloride, 773°; strontium chloride, 870°; barium chloride, 960°.

I. *The System* LiCl–NaCl–KCl.—Lithium and potassium chloride form neither compounds nor mixed crystals; the eutectic point is at 361° with 58 mols. % KCl. Lithium and sodium chlorides form a continuous series of mixed crystals, the melting point minimum being 552° with 72 mols. % LiCl. Sodium and potassium chlorides are also completely miscible, the m. p. minimum being 661° with 50 mols. % NaCl. In both these cases miscibility is incomplete at lower temperatures; in the first case the limiting miscibility curve has a maximum at 271° with 58 mols. % LiCl, and in the second case 402° with 50 mols. % NaCl. Above these maxima miscibility is complete. The ternary triangular diagram is bounded on two sides (LiCl–NaCl and NaCl–KCl) by narrow areas of complete miscibility, the remainder of the diagram being an area of incomplete miscibility, with a eutectic point at the concentration LiCl, 51·5 mols. %; NaCl, 11·5 mols. %; KCl, 3[illegible] mols. %.

II. *The System* $CaCl_2$–$SrCl_2$–$BaCl_2$. — Calcium and barium chlorides form a double salt, $CaCl_2,BaCl_2$, which is immiscible in the crystalline state with its components. There is a eutectic point at 602° with 38 mols. % $BaCl_2$. Calcium and strontium chlorides form a continuous series of mixed crystals with a minimum at 66 mols. % $CaCl_2$. At lower temperatures separation takes place, the maxi-

mum temperature on the limiting miscibility curve being 543°. Barium and strontium chlorides are also completely miscible, but on account of the dimorphism of barium chloride, the regular β-mixed crystals first separating change into a doubly refracting α-form. The course of the transition curve was determined. The ternary diagram is divided into areas of complete and incomplete miscibility by a limiting curve. In the area of incomplete miscibility is a ternary eutectic point where the double salt $CaCl_2,BaCl_2$ is in equilibrium with two ternary mixed crystal phases, rich in barium chloride and calcium chloride respectively. The ternary mixed crystals separating in the area of complete miscibility are dimorphous, and the transition surface for these mixed crystals was determined in the same way as the transition curve for the barium–strontium chloride mixed crystals. In the ternary area the existence of the binary compound $CaCl_2,BaCl_2$, crystallising at 631°, and of a ternary compound, $CaCl_2,SrCl_2,BaCl_2$, crystallising at about 500°, was established. These are the only compounds known among the chlorides of the alkaline earths. E. H. R.

Ternary Systems of Potassium Chloride, Sodium Chloride, and the Chlorides of Bivalent Metals. KURT SCHOLICH (*Jahrb. Min.*, 1920, *Beil. Bd.*, **43**, 251—294).—The equilibrium conditions in the three ternary systems formed by sodium and potassium chlorides with calcium, strontium, and magnesium chloride respectively have been investigated.

I. *The System* $CaCl_2$–KCl–NaCl.—The binary system $CaCl_2$–KCl and $CaCl_2$–NaCl were investigated by Menge (A., 1911, ii, 982), who reported the existence of compounds $KCl,CaCl_2$ and $4NaCl,CaCl_2$. Neither Lamplough (A., 1911, ii, 581) nor the present author confirms the existence of the sodium chloride compound. Sodium and calcium chlorides are practically immiscible and form a eutectic at 506° with 53 mols. % $CaCl_2$. The concentration–temperature prism of the ternary system consists of three saturation surfaces, corresponding with the separation of calcium chloride, the double salt $KCl,CaCl_2$, and mixed crystals (K,Na)Cl respectively. The double salt is immiscible with sodium chloride, and forms no compound with it. Through the double salt, the ternary system is divided into two partial systems. In the first of these there is a eutectic point in which calcium chloride, sodium chloride, and double salt are in stable equilibrium. In the second partial system, $KCl,CaCl_2$–NaCl–KCl, there is a limiting curve along which double salt and mixed crystals, (K,Na)Cl, are in equilibrium with the liquid phase. This curve reaches a minimum, where it is met by a curve crossing the mixed crystal surface from the minimum point of the binary NaCl–KCl system.

II. *The System* $SrCl_2$–KCl–NaCl.—Two compounds are formed between strontium chloride and calcium chloride, $2KCl,SrCl_2$, *E*, and $KCl,2SrCl_2$, *D*. The first compound, *E*, forms long, rhombic prisms, and has the melting point 597°; the second, *D*, has m. p.

638°, and is probably monoclinic. The compound *D* forms with sodium chloride a binary eutectic system, by which the ternary system is divided into two partial systems. The ternary diagram is very similar to the previous one, with four surfaces instead of three.

III. *The System* $MgCl_2$–KCl–NaCl.—Magnesium chloride and potassium chloride form only one compound, KCl,$MgCl_2$, the existence of the other compound reported by Menge (*loc. cit.*) not being confirmed. The compound has m. p. 487°, and crystallises in large prisms with weak double refraction. It forms with sodium chloride a binary eutectic system. Sodium chloride and magnesium chloride form two compounds, the first having the formula NaCl,$MgCl_2$, and the second probably 2NaCl,$MgCl_2$, but the evidence for the latter is indirect. The ternary system is divided into two partial systems by the binary system KCl,$MgCl_2$–NaCl. In the first partial system, $MgCl_2$–NaCl–KCl,$MgCl_2$, are five surfaces, with three invariant points, two of which are transition points and the other a eutectic. The other partial system, KCl,$MgCl_2$–KCl–NaCl, is of interest in that the eutectic mixture consists of the double salt KCl,$MgCl_2$ and two limiting mixed crystal phases of NaCl and KCl. The temperature of separation of mixed crystals of sodium and potassium chlorides is raised in presence of a third substance, through the formation of a ternary mixture. In the magnesium chloride ternary mixture the separation of the mixed crystals takes place before the end of the crystallisation process, but in the other cases, in which it was not detected, probably only after solidification is complete.

[Compare Vortisch and Jänecke, this vol., ii, 95, 96.]

E. H. R.

System Cupric Oxide, Cuprous Oxide, Oxygen. F. Hastings Smyth and Howard S. Roberts (*J. Amer. Chem. Soc.*, 1920, **42**, 2582—2607).—Cuprous oxide does not form solid solutions in cupric oxide over the temperature range where both oxides remain solid. Previous results (Wöhler, A., 1907, ii, 33) indicating such solutions may probably be explained by lack of careful temperature control, and by possible adsorption of nitrogen in solid cupric oxide giving high initial pressures. The pressure–temperature equilibrium curves for the system CuO–Cu_2O–O_2 have been established over the range in which the oxides remain solid, below the eutectic point, and above the eutectic point, where cupric oxide remains the solid phase up to 1233°. The pressure and temperature of the quadruple (eutectic) point for the system have been established from the intersection of these curves. The quadruple point lies at 1080·2° and 390 mm. pressure. The general direction of the equilibrium curve has been indicated for the system when cuprous oxide remains the only solid phase, and it has been proved that, in accordance with theory, the equilibrium pressure drops in this case with rise in temperature. Pure cupric oxide does not melt with dissociation below 1233°. J. F. S.

Statistical Mechanics Applied to Chemical Kinetics. Richard C. Tolman (*J. Amer. Chem. Soc.*, 1920, **42**, 2506—2528).—A mathematical paper in which, following the point of view of Perrin, the principles of statistical mechanics are applied to the rate of reactions in gaseous systems. It is assumed in all cases considered that the reactions proceed at a slow, measurable rate, and that they are simple, of the form $aA + bB \longrightarrow$ *products*, there being no steps, and that the mixtures are so dilute that the gas laws may be held to apply. The points treated are: (i) thermal rate of an unimolecular reaction, (ii) temperature-coefficient of the velocity of a unimolecular reaction, (iii) photochemical rate of a unimolecular reaction, (iv) temperature-coefficient of the velocity of unimolecular photochemical reactions, and (v) di- and polymolecular reactions. J. F. S.

Oxidation Pressure Limits. II. The Pressure Limit of Autoxidation considered as a Particular Case of the Inferior Limit of Explosion. W. P. Jorissen (*Rec. trav. chim.*, 1920, **39**, 715—719. Compare A., 1919, ii, 62).—The author has examined the influence of carbon dioxide on the pressure limit of phosphorescence of phosphorus and on the inferior limits of explosion of hydrogen and methane. In each case the influence of carbon dioxide is greater than that of nitrogen. Similarly, he has determined the inferior limit of explosion for acetaldehyde and its displacement by carbon dioxide. W. G.

Effect of Oxygen on the Limits of Inflammability of Inflammable Gases and Vapours. E. Terres (*J. Gasbeleucht*, 1920, **63**, 785—792, 805—811, 820—825, 836—840).—The determinations were made in a Bunte burette 19 mm. in diameter and 115—120 c.c. in capacity. Mixtures were ignited from above, and an analysis was carried out to see whether the flame had passed through the whole of the mixture. The limits were determined in air, in oxygen, and in atmospheres intermediate in composition between air and oxygen. In all cases, the lower limit differed only slightly in air and in oxygen, but the upper limit was always very much higher in pure oxygen. The results obtained in air and in oxygen were as follows. In air: carbon monoxide, 15·6—70·9; hydrogen, 9·5—65·2; water gas, 12·4—66·1; coal gas, 9·8—24·8; methane, 6·3—11·9; ethane, 4·2—9·5; ethylene, 4·0—14·0; acetylene, 3·5—52·3; light petroleum vapour, 2·1—5·0; benzene, 2·8—6·8. In oxygen: carbon monoxide, 16·7—93·5; hydrogen, 9·2—91·6; water gas, 12·6—92·0; coal gas, 10·0—73·6; methane, 6·5—51·9; ethane, 4·1—45·8; ethylene, 4·1—61·8; acetylene, 3·5—89·4; light petroleum vapour, 2·1—28·4; benzene, 2·8—29·9. W. P.

The Influence of the Solvent on the Temperature-coefficient of certain Reactions. A Test of the Radiation Hypothesis. Henry Edward Cox (T., 1921, **119**, 142—158).

Mutual Reaction of Oxalic Acid and Iodic Acid: Influence of Temperature and Dilution. GEORGES LEMOINE (*Compt. rend.*, 1920, **171**, 1094—1100).—At low temperatures and high dilutions, the decomposition of iodic acid in solution by oxalic acid, with the consequent liberation of iodine and carbon dioxide, progresses extremely slowly. The velocity of reaction increases rapidly with rise in temperature or with increase in concentration of the reagents. In all cases, there is a slight retardation at the commencement of the reaction, until the solution becomes saturated with iodine. If the solution is previously saturated with iodine, this retardation is not noticed. W. G.

Some Properties of Explosives. A Lecture delivered before the Chemical Society on December 16th, 1920. SIR ROBERT ROBERTSON (T., 1921, **119**, 1—29).

The Thermal Decomposition of Acetylene in Contact with Metallic Catalysts. E. TIEDE and W. JENISCH (*Brennstoff-Chem.*, 1920, **2**, 5—8).—Acetylene was passed at the rate of 4 litres per hour over different metallic catalysts placed in small porcelain boats inside a tube of Jena-glass, 1·4 cm. in diameter and 40 cm. long, electrically heated at temperatures up to 600°. Liquid products were collected by freezing and solution in paraffin, and estimated by weight, whilst samples of the residual gases were analysed. Two sets of metals are distinguished, "active" and "inactive." The presence of an inactive element had no effect on the temperature of decomposition, and little difference in the percentage decomposition was noticed, whether the boat was empty or contained one of these metals. At 440°, the first grey mist was formed, indicating the commencement of polymerisation, the first drops of oil beginning to collect at 540°. At 600°, the residual gases contained, on an average, 90% of unaltered acetylene. The inert elements used were Al, Sb, Pb, B, Cd, Ca, Cr, Au, C, Mg, Mo, Ag, Si, Ta, Tl, Ti, U, Bi, W, Zn, Sn, and Zr, also Pd and Pt in compact form. With the active metals, the separation of carbon and the formation of the first drops of oil, respectively, commenced at the following temperatures, and the percentage of unaltered acetylene in the residual gases (temperature of tube, 600°) were as given: Fe, 400°, 540°, trace; Co, 380°, 480°, 17·2%; Ni, 360°, 520°, 20·2%; Cu, 310°, 310°, 23·5%; Mn, 450°, 480°, 8·7%. Their action is probably due to the readiness with which these metals form carbides. Alloys were also tried. Cu–Au, Cu–Sn, Cu–Al are classed as inactive, whilst Cu–Ni was active. Finely divided Pt was also active. W. P.

Preparation of Active Hydrogenating Metals. A. BROCHET (*Bull. Soc. chim.*, 1920, [iv], **27**, 897—898).—An activated nickel may readily be prepared by heating certain of its organic salts, such as the formate or the oxalate. In the case of the formate, the decomposition is marked at 200—250°, and very rapid at 270°.

The oxalate requires a temperature of 320—380°. The nickel so obtained is not spontaneously pyrophoric at the ordinary temperature in contact with air. Cobalt and iron behave in the same manner as nickel in this method of preparation. During the decomposition of the formate by heat, there is absorption by the nickel of a small amount of the carbon dioxide produced during the decomposition. W. G.

The Preparation of Active Hydrogenating Metals in Liquid Media. A. BROCHET (*Bull. Soc. chim.*, 1920, [iv], **27**, 899—901. Compare preceding abstract).—If nickel formate is heated in cotton oil at temperatures below 150°, no change occurs, but from 160—270° the formate is decomposed and the oil undergoes partial hydrogenation. The nickel is left in an active state, and will cause the complete hydrogenation of such oil at 100° under pressure in an atmosphere of hydrogen. W. G.

The Rôle of Protective Colloids in Catalysis. I. THOMAS IREDALE (T., 1921, **119**, 109—115).

Hypotheses on the Unity of Matter. C. DE MARIGNAC (*J. Chim. Phys.*, 1920, **18**, 261—269).—A theoretical paper in which it is shown that there is nothing improbable in the hypothesis of the unity of matter, but the idea will probably always remain a purely theoretical conception. Weight is the most fundamental property of matter, and probably the only property which belongs essentially to the ultimate particles of primordial matter. Specific heat and electricity are properties of the second order which only show themselves in those groups of material particles which constitute the chemical atoms, whilst volume is a property which is determined by more or less complex groups of atoms which constitute the molecules of chemical substances. J. F. S.

Is the Existence of Atoms and Molecules Demonstrated? A. VON ANTROPOFF (*Zeitsch. angew. Chem.*, 1920, **33**, 321—324).—The question of the real existence of atoms and molecules is complicated by purely philosophical difficulties unless stated in an appropriate manner. Older and newer proofs of the existence of atoms are considered not to be convincing, but a more exact demonstration may be found in canal rays, which exhibit scintillations on a zinc sulphide screen. J. R. P.

Harmony of the Atomic Weights and Mathematics. D. DROSTE (*Pharm. Zeit.*, 1920, **65**, 822—823, 1017—1018).—The relations discovered by Schmiz (A., 1919, ii, 460) are purely mathematical and are not peculiar to atomic weights. J. R. P.

Harmony of Atomic Weights. ED. SCHMIZ (*Pharm. Zeit.*, 1920, **65**, 945).—Reply to Droste (see preceding abstract), and further speculations on the structure of atoms. J. R. P.

Is H composed of a Whole-number Part (*A*) plus an Auxiliary Part (*B*) and a Rotating Electron (*C*)? F. H. LORING (*Chem. News*, 1920, **121**, 315—318).—Hydrogen appears to be unique in not having a whole-number atom. The fractional part of its mass is relatively great. Hydrogen does not find its place properly at the heads of Groups I and VII. Its chemical activity is evidently not such as to enable it to form stable polymerides answering to known elements. There is a gap at the end of Group I that does not accommodate any radioactive element. Similarly, there are gaps below manganese which seem difficult to fill, and one of these would have to be filled by a radioactive element, which seems improbable. On the hypothesis that all elements are polymerides of hydrogen, a difficulty arises owing to the fractional value, suggesting that the fundamental unit has a mass of 1 exactly. Considering hydrogen as a complex atom composed of mass parts, $a=1{\cdot}000$, $b=0{\cdot}0077$, and c (an electron)$=0{\cdot}00055$, the parts a and b could possibly more properly be placed at the heads of Groups I and VII respectively, thus accounting for the very strong affinity between these parts and the great stability of the hydrogen complex ab. The separate parts alone might have very great affinities, especially a, which could polymerise and form the whole-number atoms. The atomic numbers of b and a might be 0 and 1, or 2 and 7. Small multiples of b might also be attached to other elements and account for irregularities in the Periodic Table. J. R. P.

The Mendeleev Series arranged and brought up to date in 1917, according to the latest published Atomic Weights. G. BOURGEREL (*Mon. Sci.*, 1920, [v], **10**, 241—242).—Jandrier (A., 1920, ii, 747) considered that there were still two unknown elements to appear in Mendeléev's series having atomic weights about 152 and 216 respectively. The present author claims to have discovered two such metals in certain minerals, and he names them ekarhodium and ekaerbium respectively. Ekarhodium gives a non-volatile chloride, which is decomposed by heat, losing chlorine. Its oxide gives salts with the alkali hydroxides.

Ekaerbium was obtained as its hydroxide, which, when calcined, gives an oxide insoluble in acids. Its hydroxide dissolves in hydrochloric acid, and on diluting the solution with water a flocculent precipitate is obtained. From the hydrochloric acid solution a black precipitate is obtained on the addition of ammonium sulphide, and the precipitated sulphide, on ignition, is converted into the oxide, which apparently has the formula E_2O_3, as, on reduction in hydrogen at 1000—1100°, it loses 3·40% of its weight. W. G.

New Periodic Classification of the Elements. GIUSEPPE ODDO (*Gazzetta*, 1920, **50**, ii, 213—245).—After referring to some of the artificialities and anomalies of the Mendeléev system, the author describes his own method of classifying the elements, this being based on the following principles. Hydrogen is placed first, lithium beneath it, and the rest of the elements in order of their

atomic weights, a new period being commenced when a pronouncedly metallic element is followed by a decidedly non-metallic element; the position of the latter, with which the new period begins, is chosen so that neon comes under helium. According to this arrangement, the non-metals form five vertical groups and are separated by the zerovalent elements from the metals, which make up eighteen vertical groups. The elements in the zerovalent vertical group are indicated by asterisks.

The eight horizontal periods comprise the following elements: (I), H alone; (II), He*, Li, Ge; (III), B, C, N, O, F, Ne*, Na, Mg, Al; (IV), Si, P, S, Cl, A*, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Ga, Ge; (V), As, Se, Br, Kr*, Rb, Sr, Yt, Zr, Nb, Mo, —, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb; (VI), Te, I, X*, Cs, Ba, La, Ce, Pr, Nd, Sa, Eu, —, Gd, Tb, Dy, —, Er, Tu; (VII), —*, Yb, —, Lu, —, Ta, W, —, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, [Th-D, Ra-D, -E, -F = Po, AcD], [Th-B, -C_1, -C_2, Ra-B, -C_1, -C_2, AcB and C], [Th-A, Ra-A, Ac-A]; (VIII), [Em-Th, Em-Ra, Em-Ac]*, [Th, Ra, Ac], [M-Th 1 and 2, Ra-Th, Ux, Uy and Io, Ra-Ac, and Ac], [Th, U_2], U.

The advantages of this system in bringing out both the physical and chemical analogies, not only among the groups, but also among the periods, are discussed. T. H. P.

Periodic Classification of the Elements. J. R. PARTINGTON (*Chem. News*, 1920, **121**, 304).—A spiral representation of the periodic system, similar to that of Nodder (this vol., ii, 38), but showing radioactive changes, isotopes, and the Fajan's rule, is described. J. R. P.

Periodic System of the Elements from the Point of View of the Theory of Radioactive Disintegration. F. KIRCHHOF (*Physikal. Zeitsch.*, 1920, **21**, 711—718).—A theoretical paper in which the considerations previously published (A., 1920, ii, 611) are further developed. It is shown that the atomic weights of the elements may be calculated by means of the formula $A = 2(M + I)^2$, in which M is the atomic number and I the isotope number. It is shown that the anomalous atomic weights of the pairs of elements, argon–potassium; cobalt–nickel; tellurium–iodine, are to be explained by the fact that the element first named has a larger isotope number than the second, and since the isotope number depends, in part, on the relative period of existence of the isotopes, it follows that in the first-named element the isotope with largest atomic weight has the longest life, and consequently the atomic weight of the isotope mixture is correspondingly larger, whilst in the case of the second element the isotope with the smaller atomic weight has a longer life than the corresponding isotope of the first-named element; consequently, the atomic weight of the second element is smaller, and so the anomaly comes into being. On plotting curves of the isotope number against the atomic number of the elements with even atomic number in one curve and those of odd atomic number in another curve, it is found that up to germanium the

curve of the even elements lies below the odd elements, thereafter up to molybdenum the two curves run side by side and very close together, and beyond molybdenum the curve of the even elements lies above that of the odd elements. The author shows that many even elements show a very close analogy to the next odd element. A list of such pairs is given, and a discussion is entered into as to their origin. An arrangement of the periodic system is put forward which in many respects is similar to that put forward by Crookes and by Soddy. J. F. S.

Standardisation of Weights. A. J. HOPKINS, J. B. ZINN, and HARRIET ROGERS (*J. Amer. Chem. Soc.*, 1920, **42**, 2528—2531).—A method is described, which is a slight modification of that published by Richards (A., 1900, ii, 534), for redistributing the error accumulated in a set of calibration weighings over the whole of the weights concerned, and not allowing it all to fall on the heaviest weight employed. The method makes use of a box of standards, 100 mg., 1, 5, 50, and 500 grams. J. F. S.

Modified Soxhlet Extraction Apparatus. OSKAR HAGEN (*Chem. Zeit.*, 1921, **45**, 19).—The ordinary siphon tube of the Soxhlet apparatus is dispensed with, and the stem of the apparatus is bent into a ring-shaped trap, which is provided with a two-way tap. The condensed solvent falls from the condenser into a thimble containing the substance to be extracted, and fitted in the cylindrical part of the apparatus, and then passes down the stem, through the tap, and into the extraction flask. By turning the tap, the solvent may be drawn off from the ring-shaped trap as desired. W. P. S.

Sulphuric Acid Concentrator and Vacuum Pump. O. MAASS (*J. Amer. Chem. Soc.*, 1920, **42**, 2571—2574).—The apparatus described is useful for concentrating solutions under reduced pressure. It has the advantage over a mercury pump that the vapours removed from the solution are absorbed by the sulphuric acid, and so the vacuum is kept down to the vapour pressure of sulphuric acid, and not to that of the liquid evaporating. The liquid to be concentrated is placed in bulbs, which are connected to a large, cylindrical vessel filled with glass tubes, below which is placed the sulphuric acid reservoir. The apparatus is exhausted to the point to which a Geissler pump will take it, and then the sulphuric acid is forced into the evacuated cylindrical vessel by an automatic control (A., 1919, ii, 104), which has the effect of absorbing vapours, forcing the non-absorbable gases from the apparatus, and moistening the glass rods in the cylindrical vessel with sulphuric acid. The control then withdraws the sulphuric acid into the reservoir, which improves the vacuum. This process then goes on repeatedly until the evaporation or concentration is completed. J. F. S.

Device for Preventing Back-flow of Water from Water-pumps. HANS DORSCH (*Chem. Zeit.*, 1921, **45**, 32).—The handle of a glass tap is fixed rigidly in a clamp so that the tubes on either side of the tap are in a horizontal position when the tap is open; the tube on one side of the tap is connected by a piece of rubber pressure tubing with the vessel from which the air is to be exhausted, whilst the tube on the other side of the tap is bent slightly downwards and passed through a rubber stopper closing a flask. A second tube passes through the stopper and reaches to the bottom of the flask, the outer end of this tube being connected by a piece of rubber tubing to the water-pump. If the water pressure decreases, water flowing back from the pump enters the flask, and the additional weight causes the flask to descend, thereby closing the tap; when the water pressure increases, water is drawn from the flask, the latter rises, and the tap is opened, thus placing the pump once more in connexion with the vessel. W. P. S.

Expulsion of a Gas from its Solution by Changing its Solvent. S. GENELIN (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 147).—Ethyl chloride gas, generated by dropping warm water into a small amount of ethyl chloride, may be conducted into alcohol until the evolution of bubbles indicates a saturated solution. By shaking the alcoholic solution with much water, the insolubility of the gas in water is indicated by the evolution of gas bubbles.
CHEMICAL ABSTRACTS.

The Preparation of Nitrogen Peroxide from Air with the Spark from a Weak Induction Coil. S. GENELIN (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 146—147).—The spark from a weak induction coil, if discharged from platinum electrodes 1—2 mm. apart in a eudiometer tube standing vertically with open end up, will generate sufficient nitrogen peroxide to be recognisable by colour in half an hour, provided the air in the tube is previously well dried by sulphuric acid for twenty-four hours. The gaseous contents of the tube, if dissolved by shaking with a very little water, will give the test for nitrous acid. CHEMICAL ABSTRACTS.

The Ignition of Phosphorus under a Bell Jar standing over Water. H. REBENSTORFF (*Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 18—20).—Small pieces of phosphorus are placed in a porcelain dish floating on water under a bell jar. The stopper of the bell jar carries a glass tube sealed at the upper end and containing tin which has been melted together after being placed in the tube in the form of fine granules; at the lower end, a tube of diameter large enough to slip over the first is fastened by a wire or cord so that the length of the tube is adjustable. After placing the tube so that it rests directly over the phosphorus, the upper part of it is heated until a drop of the hot tin falls on the phosphorus and ignites it. CHEMICAL ABSTRACTS.

Inorganic Chemistry.

Properties of Pure Hydrogen Peroxide. I. O. MAASS and W. H. HATCHER (*J. Amer. Chem. Soc.*, 1920, **42**, 2548—2569).—Pure hydrogen peroxide is obtained as follows: 3% hydrogen peroxide, obtained from barium peroxide, is concentrated to 30% by means of a sulphuric acid concentrator (Maass, this vol., *ii*, 104). It is then distilled at very low pressure to remove the non-volatile impurities. A self-acting sulphuric acid pump is used at this stage to keep the pressure down. A further concentration by the sulphuric acid concentrator at 0° raises the concentration to 90%, but above this point it is not possible to go, because of the high vapour tension of the peroxide. The final product, 100% hydrogen peroxide, was obtained by fractional solidification and melting. Adopting this method, and using all the precautions noted by the authors, a yield of 50% of pure hydrogen peroxide may be obtained from the 3% solution. The pure material is found to have the following physical properties: m. p. −1·70°, whilst a 96·7% solution melts at −4·00; density of liquid, at −12·13°, 1·4774; −6·23°, 1·4705; −0·53°, 1·4638; 1·20°, 1·4617; 5·55°, 1·4570; 8·30°, 1·4541; 12·60°, 1·4490; 15·30°, 1·4465; and 19·90°, 1·4419; density of solid, −4·45°, 1·6434; −7·45°, 1·6437; viscosity, 0·04°, 0·01828; 11·90°, 0·01456; 12·20°, 0·01447; 19·60°, 0·01272; surface tension, 0·2°, 78·73; 6·2°, 77·79; 11·0°, 77·51; 13·9°, 76·47; and 18·2°, 75·94 dynes; association factor, 3·48; specific heat of liquid, 0—18·5°, 0·5730; −32·0—18·0°, 0·5697; specific heat of solid, −9·0—17·87°, 0·4701; latent heat of fusion, 73·91 cal.; refractive index (*D*), 22°, 1·4140; molecular refractive power, 5·900. Hydrogen peroxide is very slightly soluble in ether, it dissolves many normal salts readily, and attacks glass. Pure hydrogen peroxide explodes violently when a piece of sodium is added; it whitens, but does not permanently destroy, living skin; it does not decompose when kept at 0°. J. F. S.

Properties of Pure Hydrogen Peroxide. II. O. MAASS and O. W. HERZBERG (*J. Amer. Chem. Soc.*, 1920, **42**, 2569—2570. Compare preceding abstract).—The freezing-point curve of mixtures of hydrogen peroxide and water has been determined for the whole range of concentration. It is shown that only one compound, $H_2O_2,2H_2O$, exists; this has a melting point −51°, and corresponds with 48·6% of hydrogen peroxide. J. F. S.

Molecular State of Water Vapour. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1920, **42**, 2477—2482).—A theoretical paper in which the contradictory conclusions of Bose (A., 1908, ii, 577) and Oddo (A., 1915, ii, 683) with regard to the molecular state of water vapour are discussed, in view of the fact that the unimole-

cular nature of this substance has been questioned, the existence of double molecules at high temperatures and of spontaneous ionisation at low temperatures being assumed. It is shown that the evidence in support of the equilibria $H_2O \rightleftarrows H^{\cdot} + OH'$ and $2H_2O \rightleftarrows (H_2O)_2$ is in each case entirely insufficient, and that the abnormalities in the vapour densities of normal substances at their boiling points are similar to that in water vapour at 100°. Such abnormalities practically vanish on applying the corrections for deviations from the perfect gas laws. An equation of state correction is similarly necessary in gas reactions at high pressures, in calculations on dissociation in the vapour state, and in Dumas or Victor Meyer vapour-density determinations. J. F. S.

The Purification of Air Containing certain Toxic Gases. A. DESGREZ, GUILLEMARD, and SAVÈS (*Compt. rend.*, 1920, **171**, 1177—1179; *Chim. et Ind.*, 1920, **4**, 514—517).—For the removal of chlorine at a concentration of 1 in 2000, a solution of 220 grams of sodium thiosulphate and 175 grams of sodium carbonate in 1000 c.c. of water is sprayed in with a Vermorel sprayer. For a mixture of carbonyl chloride and chlorine a 12% solution of sodium carbonate is the best spray fluid. A fluid containing 240 grams of sodium polysulphide and 140 c.c. of soap boilers' lye in 1 litre is efficient for removing chlorine, carbonyl chloride, chloromethyl chloroformates, acraldehyde, bromoacetone, cyanogen chloride, chloropicrin, and benzyl chloride, bromide, or iodide. W. G.

History of the Knowledge of Combustion. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1920, **33**, 301).—A bibliographical résumé of the knowledge of combustion in ancient and mediæval times. W. P. S.

The Mechanism of some Combustions. H. VON WARTENBERG and B. SIEG (*Ber.*, 1920, **53**, [*B*], 2192—2202).—The correctness of the assumption that reaction between two substances is preceded by the formation of an unstable additive compound is now proved in the case of certain combustions.

Carbon monoxide, for example, must be moist before it will react with oxygen at ordinary flame temperatures. The amount of water necessary to promote explosion of the ideal mixture is just the same, whether the oxygen is provided as oxygen gas or as nitrous oxide, and is approximately that quantity which corresponds with a partial pressure of 0·5 mm. Moreover, the presence of hydrogen may be demonstrated in a carbon monoxide flame, which, in addition to Wieland's proof of the production of formic acid (A., 1912, ii, 347), completely supports Dixon's theory of the mechanism of the combustion (T., 1886, **49**, 94), thus: (1) $CO + H_2O = H \cdot CO_2H$; (2) $H \cdot CO_2H = CO_2 + H_2$; (3) $H_2 + O_2 = H_2O_2$; (4) $H_2O_2 = H_2O + O$. In the experiments to prove the first reaction, the explosive gases were allowed to stream from a water-gasometer, through a coil immersed in a Dewar vessel, then through a short tube packed with

brass filings to prevent back-fire, and into a tube provided with platinum wires to give a spark about 1 cm. long. After drying the apparatus at 300—400° by means of air circulated over phosphoric oxide, alcohol and solid carbon dioxide were placed in the Dewar vessel, and the temperature was gradually allowed to rise until the gases were moist enough to explode. Explosion took place at about −23°. The sparks must be regular in order to get comparative results, for combination, of course, takes place at every spark, and whether the explosion is propagated throughout the gas or not depends on the amount of heat developed. In an experiment in which the explosion-chamber was heated at one spot by a blowpipe flame, the gases reacted over the hot surface even when the temperature of the drying coil was −80°, giving a flame which slowly wandered into the colder parts and was soon extinguished. The presence of hydrogen in a carbon monoxide flame was demonstrated by burning the gas in a Bunsen burner with quartz tube and holding in the flame a platinum tube attached to an exhausted mercury manometer. A fall in the column of mercury indicated diffusion of hydrogen into the platinum tube, and was only observed if the carbon monoxide or air supplies were moist.

The combustion of hydrogen proceeds *via* the formation of hydrogen peroxide. It appeared that this might be demonstrated by preventing the explosion of hydrogen and oxygen mixtures by substances unfavourable to the formation of hydrogen peroxide. The mixtures were therefore passed through various liquids, warmed to such temperatures that the vapour carried forward was sufficient to prevent explosion. The necessary partial pressures in % of the total pressure are as follows: CH_2O, 68; CS_2, 84·2; HCl, 65·5; NH_3, 63·4; SO_2, 58·3; HCN, 59·3; MeOH, 52·0; H_2S, 50·0; Me·CHO, 35·5; Et_2O, 33·4; EtCl, 31·9; EtSH, 30·5; Me_2O, 29·6; $EtNH_2$, 27·7; Pr_2O, 25·4; Me_2CO, 21·3; C_6H_{14}, 19·7; $MeCO_2Et$, 17·3; C_7H_8, 13·1; Me_3N, 14·2; C_6H_6, 13·6. Obviously, these results throw no light on the point in question, for it is scarcely conceivable that benzene should be so much more effective than formaldehyde. The formation of hydrogen peroxide was approximately determined quantitatively by passing a mixture of oxygen and hydrogen in the ratio 9:1 through a quartz tube narrowed to a capillary, part of which was heated and the remainder cooled, and allowing the products to collect in a weighed receiver in a freezing mixture. The rate of flow of the gases, the temperature, the weight of water and hydrogen peroxide (permanganate titration) formed, and the amount of ozone in the issuing gases (iodine titration) were determined. Using oxygen and water vapour only, no hydrogen peroxide and very little ozone could be found, whereas the amount of hydrogen peroxide obtained by burning hydrogen and oxygen was about one million times as great as that demanded from the equation $H_2O + \frac{1}{2}O_2 \rightleftharpoons H_2O_2$, and, moreover, decreased, instead of increased, with rise of temperature. It appears, therefore, that the union of hydrogen and oxygen at 600—1000° so proceeds that hydrogen peroxide is first formed in considerable concentration, then quickly

decomposes into water and oxygen, atoms of the latter uniting to a certain extent to form ozone, which decomposes more slowly than hydrogen peroxide and is found in greater concentrations.

A hint of the production of a peroxide-like substance was also obtained in the case of cyanogen, and the combustion of methane (Bone and Wheeler, T., 1902, **81**, 535) may be interpreted in a similar manner. J. C. W.

Simple Form of Kipp's Apparatus for the Generation of Hydrogen Sulphide. V. B. CONNELL (*Pharm. J.*, 1921, **106**, 17).—A wide-mouthed bottle is closed with a rubber stopper through which pass a delivery tube and a vertical tube reaching to the bottom of the bottle; the end of the delivery tube is fitted with a length of rubber tubing and a spring clip. The outer end of the vertical tube extends just through a rubber stopper closing a second similar bottle which is placed in an inverted position over the first. The ferrous sulphide is placed in the first bottle, and the inverted bottle serves as a reservoir for the acid when the apparatus is not in use. A bent tube, extending to the top of the inverted bottle, allows air to enter or escape according to the change in level of the acid. W. P. S.

Trithiocarbonates and Perthiocarbonates. ERNEST WICKHAM YEOMAN (T., 1921, **119**, 38—54).

Preparation of Selenium Oxychloride. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1920, **42**, 2498—2500).—A number of methods are described for the preparation of selenium oxychloride, selenium monochloride, and selenium tetrachloride. Selenium monochloride is prepared by suspending powdered selenium or powdered minerals containing selenium in carbon tetrachloride saturated with chlorine. The selenium is converted into the monochloride in the cold, and dissolves in the carbon tetrachloride, whilst the chlorides of other elements present are insoluble. The monochloride is therefore obtained by filtration and distillation of the carbon tetrachloride.

Selenium tetrachloride is prepared by saturating a cold solution of the monochloride in carbon tetrachloride or chloroform with chlorine. The tetrachloride is insoluble, and precipitates as rapidly as it is formed as a white powder.

Selenium oxychloride is prepared by adding dry selenium dioxide to a suspension of selenium tetrachloride in carbon tetrachloride. Reaction takes place in the cold, and the oxychloride dissolves in the carbon tetrachloride, from which it may be obtained by distillation, b. p. 176·4°. A perfectly pure product is obtained by fractionation under slightly reduced pressure. The oxychloride can also be obtained by adding the theoretical quantity of water to a suspension of the tetrachloride in carbon tetrachloride, according to the equation $SeCl_4 + H_2O \longrightarrow SeOCl_2 + 2HCl$. It may also be prepared from the compound $SeO_2,2HCl$. This substance is obtained by

treating selenium dioxide with dry hydrogen chloride at low temperatures when an amber-coloured liquid is formed. On mixing this liquid with phosphoric oxide or calcium chloride and distilling, the oxychloride passes off. The reaction may also be effected by mixing selenium dioxide with the dehydrating agent and passing in hydrogen chloride in the cold and then distilling off the oxychloride.

J. F. S.

The Sub-iodide of Tellurium, TeI_2. The System Iodine–Tellurium. A. DAMIENS (*Compt. rend.*, 1920, **171**, 1140—1143).—From a thermal study of mixtures of tellurium and iodine in varying proportions it is shown that the so-called tellurium subiodide, TeI_2, is not a definite compound, but is a mixture of two substances, namely, the tetraiodide and a solid solution of tellurium and the tetraiodide. The product, having the composition TeI_2, when melted and allowed to cool, deposits first of all the tetraiodide at 215°, and on further cooling the eutectic mixture begins to deposit at 170·3° and continues until complete solidification is reached. The curve only indicates one definite compound, the tetraiodide, TeI_4.

W. G.

Preparation of Hydrogen Triarsenide of High Percentage Purity, and its Estimation. H. THOMS and L. HESS (*Ber. Deut. Pharm. Ges.*, 1920, **30**, 483—489).—Pure hydrogen triarsenide is conveniently obtained by the action of water or acids on calcium arsenide (compare Lebeau, A., 1899, ii, 288). The difficulty and danger of preparing the latter substance can be entirely obviated by adding a neutral diluent, such as sand (5·5 kilo.) to the mixture of powdered arsenic (3·1 kilo.) and coarse calcium filings (2·4 kilo.). This mixture is placed in a container made of sheet iron, bolted together in such a way that it can be entirely opened up at the end of the experiment to remove the solid cake of arsenide. The container is placed within a second vessel with an air-tight cover, which during the combustion is replaced by an asbestos cover with a hole in the centre. The combustion is started by means of a magnesium–potassium chlorate mixture, and slowly extends throughout the entire mass, giving rise to an intense glow, but no flame and formation of but little arsenious oxide. When cold, the arsenide is removed and ground to a coarse powder, and may be then used, instead of sand, in the same proportion, as diluent in succeeding preparations. The evaluation of calcium arsenide by estimation of the hydrogen arsenide evolved on treatment with water is carried out in a brine-charged nitrometer connected at the top with a stoppered bulb absorption vessel containing copper chloride solution, and at the base with a closed decomposition vessel, also filled with brine and containing a weighed quantity of the arsenide in a small weighing bottle closed with a rubber stopper. When all air has been removed the stopper is knocked out of the weighing bottle, and the hydrogen arsenide and hydrogen evolved collected in the nitrometer. The percentage

of hydrogen arsenide in the gas is estimated by passing it into the copper chloride absorption bulb and shaking vigorously, the residual hydrogen being passed back into the nitrometer and measured. Calcium arsenide prepared as above described gives about 37—38% of hydrogen arsenide as compared with 58% theoretically. The remainder of the arsenic appears, probably as solid hydrogen arsenide, as a brown powder in the reaction vessel. The gaseous hydrogen arsenide usually contains about 0·004% by weight or 14% by volume of hydrogen. Aqueous solutions of the gas undergo rapid decomposition, with the formation of arsenic, which remains in colloidal solution. The decomposition can be followed by titration of the solution with $N/100$-iodine. The oxidation occurs in two phases: $AsH_3 + 3I_2 + 3H_2O = H_3AsO_3 + 6HI$, and then, after rendering alkaline with potassium hydrogen carbonate, the usual oxidation to arsenic acid. G. F. M.

Softening of Carbon. JULIUS GMACHL-PAMMER (*Monatsh.*, 1920, **41**, 467—476).—The results of the author's experiments on the softening of carbon when heated show that impurities exert an influence, impure carbon being distinctly, although not considerably, more flexible than the pure element. Graphite rods soften only at a much higher temperature than arc carbons; this observation is confirmed by the fact that protracted heating of arc carbons, which converts the latter into graphite, raises the softening point to a marked extent (compare Plotnikow, *Physikal. Zeitsch.*, 1918, **19**, 520; 1919, **20**, 25). T. H. P.

The Preparation of Artificial Diamonds. F. FISCHER (*Brennstoff-Chem.*, 1921, **2**, 9).—Under pressures which are not abnormally high the separation of carbon in the form of diamond (a non-conductor of electricity) can take place only below 700°; otherwise it appears as graphite (which is a conductor). This explains the small size of the diamonds obtained by Moissan. At 700° the iron containing the carbon in solution had already solidified, so that the carbon could only separate in the form of tiny crystals. Larger diamonds could possibly be obtained by the utilisation of a substance in which carbon was readily soluble, but which would still be molten at 700°. W. P.

The Methods of Investigating the Molecular Condition of Silicate Fusions. H. E. BOEKE (*Jahrb. Min.*, 1914, *Beil. Bd.*, **39**, 64—78).—A review of the methods available for the determination of the molecular weight of fused silicates, and of the work so far published on the subject by different investigators. The methods discussed include those depending on determinations of surface tension, electrical conductivity, diffusion, and depression of freezing point. E. H. R.

Inflammability of Jets of Hydrogen and Inert Gas (Helium). P. G. LEDIG (*J. Ind. Eng. Chem.*, 1920, **12**, 1098—1100).—Experiments were made to determine the maximum

amount of hydrogen which could be used with helium in balloons without losing the advantage of non-inflammability. Under the most favourable conditions, a jet of helium containing more than 14% of hydrogen can be ignited in air, but from 18 to 20% of hydrogen may be mixed with helium without producing a mixture which will burn with a persistent flame when issuing from an orifice under the conditions prevailing in balloon practice. A mixture containing more than 20% of hydrogen cannot be used with safety. W. P. S.

Hydrolysis of the Silicates of Sodium. ROBERT HERMAN BOGUE (*J. Amer. Chem. Soc.*, 1920, **42**, 2575—2582).—The hydrolysis of various silicates of sodium in aqueous solution has been determined by the electrometric measurement of the hydrogen-ion concentration. The results show that if the conclusions reached by earlier investigators, to the effect that dilute solutions of sodium silicate are highly hydrolysed, are to be accepted, then it follows from the present work that the electrometric hydrogen-ion method is unsuitable as a means of measuring such hydrolysis. The reason for this appears to be in a possible ability of the colloidal silica to adsorb or otherwise destroy the effect of a certain proportion of the hydroxyl ions in the solution. The effect of dilution on this adsorptive or retarding influence follows closely the same laws as the effect of dilution on hydrolysis. The hydrogen-ion determination may serve, however, as a measure of the actual alkalinity of the dispersed phase. If the assumptions made in the present paper are entirely justified, then it follows that the hydrolysis of the silicates of sodium is much lower in dilute solutions than has been held to be the case, ranging from 1·58% to 28·43% at a dilution of 100 litres per gram-mol. in the silicates, which vary in their $Na_2O : SiO_2$ ratio from 1 : 4 to 1 : 1. Sodium metasilicate is the most highly hydrolysed salt, and the degree of hydrolysis decreases the larger the amount of silica in the silicate. J. F. S.

Carbonates. II. HANS LEITMEIER (*Jahrb. Min.*, 1916, *Beil. Bd.*, **40**, 655—700. Compare A., 1910, ii, 503).—Experiments are recorded on the crystallisation of calcium and magnesium carbonates, in an investigation on the genesis of deposits of these carbonates and of dolomite. In presence of magnesium sulphate, calcium carbonate crystallises at 20° from water saturated with carbon dioxide only in the rhombic form (aragonite); 0·9% of magnesium sulphate in solution is sufficient to inhibit the appearance of calcite. The opinion of Vaubel (A., 1912, ii, 1180) that there is a chemical difference between aragonite and calcite, the former containing hydroxyl in the form of basic carbonate, is shown experimentally to be incorrect.

Solutions saturated with magnesium hydrogen carbonate deposit at the b. p. a basic carbonate, $Mg_4C_3O_{10},6H_2O$, in the form of slender needles. This basic carbonate is deposited alone at temperatures down to 65°, but at 60° it appears mixed with larger prismatic

crystals of the trihydrate, $MgCO_3,3H_2O$. Below 55° the trihydrate alone is formed, down to about 6—10° (compare A., 1910, ii, 49). The pentahydrate, $MgCO_3,5H_2O$, is very unstable at ordinary temperatures, becoming dehydrated to the trihydrate. It is identical with the mineral lansfordite. Many attempts to synthesise crystalline magnesite were made without success. After a long discussion it is concluded that the mineral is probably of marine origin. Amorphous magnesite is formed by the decomposition of magnesium silicates by carbonic acid. Experiments lasting over several months were made on the solubility of serpentine and olivine in water containing varying proportions of carbon dioxide, and it was proved that the minerals are attacked with formation of silica and magnesium carbonate. The latter probably first appears in nature as the trihydrate, and undergoes slow transformation into the amorphous, anhydrous form. Numerous attempts were made to obtain synthetic dolomite by crystallisation of calcium and magnesium carbonates under different conditions, but without success. Probably mixtures of the composition of dolomite are formed from seawater, and undergo recrystallisation into dolomite by processes not yet discovered.

The following solubilities in water, saturated with carbon dioxide, at the ordinary temperature, were determined: crystallised magnesite, 0·08 gram; amorphous magnesite, 0·22 gram; and dolomite, 0·11 gram per litre. E. H. R.

A Complex Combination of Thallium and Hydrofluoric Acid. BARLOT (*Compt. rend.*, 1920, **171**, 1143—1145).—When thallium is dissolved in hot dilute hydrofluoric acid and the solution evaporated to dryness, a *compound*, H_2TlF_3, is obtained, which crystallises from water in white, elongated prisms. On heating, it gives off hydrogen fluoride, and its aqueous solution is acid, but does not attack glass, the fluorine ion being masked. The neutralisation curve indicates that this new complex acid can form two types of salts, $KHTlF_3$ and K_2TlF_3. The specific coefficient of magnetisation is 50% higher than the value calculated from the elements. W. G.

The Reaction between Nitric Acid and Copper. LANCELOT SALISBURY BAGSTER (T., 1921, **119**, 82—87).

Solubility of Cupric Hydroxide in Concentrated Sodium Hydroxide Solution. ERICH MÜLLER (*Zeitsch. angew. Chem.*, 1920, **33**, 303—305).—Cupric hydroxide dissolves in concentrated sodium hydroxide solution, yielding a violet-blue coloured solution; in the case of 48% sodium hydroxide solution, the latter may dissolve about 30 grams of copper per litre. The solution is not, however, stable. The author discusses the reaction, particularly as regards the cause of the decomposition, state of the dissolved copper, etc. W. P. S.

Density of Aluminium from 20° to 1000°. J. D. EDWARDS and T. A. MOORMANN (*Chem. Met. Eng.*, 1921, **24**, 61—64).—The density of liquid metals that do not attack quartz may be determined by ascertaining the apparent loss in weight of a hollow quartz cylinder loaded with iron or nickel and immersed in the molten metal. Aluminium, however, rapidly attacks quartz, especially at temperatures above 700°; the authors, therefore, used a densimeter consisting of a small graphite cylinder with a tightly fitting lid enclosed in a larger cylinder, filled to within ½ in. of the top of the smaller cylinder with molten aluminium in which a thermocouple was fixed. The smaller cylinder was filled with the molten metal, the lid screwed down, and the whole apparatus brought slowly to the desired temperature. After removing the metal that exuded from the opening provided in the lid, the metal in the outer cylinder was poured out, the apparatus allowed to cool, and the metal in the inner cylinder weighed. The volume of the cylinder had previously been determined by weighing the amount of mercury required to fill it, and due allowance was made for the expansion of the graphite. By this means it is found that liquid aluminium (99·75% Al), at its melting point (658·7°), had $D^{658 \cdot 7}$ 2·382, whilst the annealed solid metal has D^{20} 2·703. The density at temperatures above 658° is given by the equation $D_t = 2{\cdot}382 - [0{\cdot}000272(t - 658)]$. The shrinkage on solidification is approximately 6·6%. A. R. P.

Hydrates of Aluminium Nitrate. KENZO INAMURA (*Mem. Coll. Sci. Kyōtō* 1920, **4**, 105—112).—See A., 1920, ii, 625.

The Transformation of Aluminium Silicates by Salt Solutions at Temperatures up to 200°. HANS SCHNEIDERHÖHN (*Jahrb. Min.*, 1915, *Beil. Bd.*, **40**, 163—228).—A statistical study of the work of Lemberg, Thugutt, and others, who carried out a very large number of analyses of the products obtained by the action of different salt solutions on many natural and synthetic aluminium silicates at temperatures up to 200°. It is shown that by the action of salt solutions on felspars, leucite, nepheline, zeolite, hauyn, sodalite, scapolite, as well as on amorphous synthetic silicates and on kaolin, allophane, etc., silicates of the type $R''O,Al_2O_3,xSiO_2,yH_2O$ are obtained as primary transformation products, in which the molecular ratio of base $R''O$ to alumina is always 1 : 1. By continued action of alkali hydroxides or carbonates, the product is left with $2SiO_2$. The amount of water present depends on the nature of the base and on the physical condition of the original material. In these primary products the base $R''O$ is readily exchanged by the action of other salt solutions with formation of secondary products. The silica content remains constant during such secondary transformations. Another type of compound is formed by the action on the silicates enumerated above of highly concentrated sodium hydroxide or carbonate solutions. The products are of the type $Na_2O,Al_2O_3,2SiO_2,yH_2O,zNaX$, where

X may be any organic or inorganic acid radicle. The molecular sum of the water and the added salt NaX always bears a simple ratio to the alumina. By the secondary action of other salt solutions the compounds of this type are decomposed, the combined salt NaX being detached and products formed similar to the secondary products of the first type. The physical and chemical properties of these substances are fully discussed, and their close relationship to the permutites is emphasised, particularly their amorphous character and easy susceptibility to basic exchange. E. H. R.

The Reduction of Permanganate by Arsenious Acid. MAX GELOSO (*Compt. rend.*, 1920, **171**, 1145—1148).—When potassium permanganate is reduced in acid solution by arsenious acid a green solution is obtained, from which, on keeping, a reddish-brown precipitate is obtained. The manganese is reduced to a state corresponding with an oxide, Mn_3O_5, which, however, does not show the characteristics of a definite oxide. It is possible that the reduced solution contains a double salt, comprising a colourless manganous salt and a green, unstable salt in which the oxide, MnO_2, functions as a base (compare Frémy, this Journ., 1877, i, 52). W. G.

Electrolytic Preparation of Sodium Permanganate. C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1920, **24**, 608—616).—A manganese anode containing 92·0% of manganese was used, the impurities being mainly iron, silicon, and carbon. The cathode was a perforated platinum plate. In all cases 350 c.c. of electrolyte are used, containing 10 grams of sodium hydroxide per litre. The addition of excess of calcium hydroxide to the solution raises the current efficiency at 25° from 16·4% to 32·8%. The calcium hydroxide appears to form a film over the cathode, which acts as a diaphragm. The current efficiency is greatest (38%) at a current density of 13 amperes per sq. dcm. at low temperatures (8°). It appears that the efficiency increases as the temperature decreases. The higher the valency with which the metal goes into solution the higher is the discharge potential. J. R. P.

Solubility of Metals in Acids containing Formaldehyde. ROGER C. GRIFFIN (*J. Ind. Eng. Chem.*, 1920, **12**, 1159—1160).—The presence of 1% of formaldehyde in dilute sulphuric acid or hydrochloric acid (1:1) decreases very considerably the solvent action of these acids on wrought iron, cast iron, and steel; the effect is less in the case of 10% nitric acid, possibly on account of secondary reactions. The solvent action of the acids on brass, tin, solder, and nickel is not greatly affected by the presence of formaldehyde. W. P. S.

Chemistry and Crystallography of some Fluorides of Cobalt, Nickel, Manganese, and Copper. FLOYD H. EDMINSTER and HERMON C. COOPER (*J. Amer. Chem. Soc.*, 1920, **42**, 2419—2433).—The fluorides of cobalt, nickel, manganese, and

copper can be prepared by dissolving either the hydroxide or the carbonate of the metal in hydrofluoric acid. The same derivative is obtained whichever compound is used. In all cases a crust-like product was obtained when the original solution was evaporated. From the slightly acidified (HF) water extract, crystals of the acid fluorides were obtained, which have the general formula

$$MF_2,5HF,6H_2O.$$

These fluorides are not permanent in the air, but decompose, losing hydrogen fluoride, and in the case of the copper compound water is also lost. The formation of the hydrated crystalline crust is distinct from that of the hydrated acid crystals. In this crust the ratio of metal to fluorine for the cases cobalt and nickel was found to be approximately 1 : 2 with a varying water content. The crust differs from the crystals in solubility and form, as well as in composition. The acid fluorides of cobalt, nickel, and manganese form rhombohedral crystals with prismatic cleavage, parallel extinction, and uniaxial positive character, and therefore constitute an isomorphous series. The acid fluoride of copper crystallises in the monoclinic system; it is pleochroic, and shows three cleavages parallel to three faces. The salts have the following densities: cobalt, 2·0445; nickel, 2·006; manganese, 1·921; and copper, 2·4055. From the original preparation of copper fluoride, small crystals of the normal fluoride, $CuF_2,2H_2O$, were obtained, which were too small for measurement. On recrystallising these from water they reverted into the acid fluoride. J. F. S.

Properties of Subsidiary Valency Groups. I. Molecular Volume Relationships of the Hydrates and Ammines of some Cobalt Compounds. II. Subsidiary Group Mobility as Studied by the Heat Decomposition of some Cobaltammines. George L. Clark, A. J. Quick, and William D. Harkins (*J. Amer. Chem. Soc.*, 1920, **42**, 2483—2498).—The specific gravity of a number of cobalt derivatives has been determined at 25° with the object of ascertaining the influence of the volume of the constituents on the stability of the cobalt ammines and hydrates. The methods of preparation and analysis are described in all cases. The following values of the specific gravity at 25° are recorded: anhydrous cobaltous chloride, 3·356; cobaltous chloride hexahydrate, 1·924; cobaltous chloride dihydrate, 2·477; hexamminecobaltous chloride, 1·497; pentamminecobaltous chloride monohydrate, 1·559; pentamminecobaltous chloride, 1·580; tetramminecobaltous chloride, 1·593; diamminecobalt chloride, α 2·097, β 2·073; pentamminecobaltic chloride, 1·819; aquopentamminecobaltic chloride, 1·776; hexamminecobaltic chloride, 1·744; anhydrous cobaltous sulphate, 3·710; cobaltous sulphate heptahydrate, 1·948; cobaltous sulphate hexahydrate, 2·029; cobaltous sulphate tetrahydrate, 2·368; pentamminecobaltous sulphate, 1·703; and tetramminecobaltous sulphate dihydrate, 1·805. The molecular volume is calculated in each case, and from these values the apparent volume of the subsidiary group in the compound is calcu-

lated, and the percentage compression. It is shown that water and ammonia in subsidiary groups have volumes in the ratio 14·265 : 19·33. The volume of the ammonia group in the cobaltous chloride ammines increases in passing from the hexammine to the diammine. *Decammine cobaltous chloride* has been prepared as a brown powder, D 1·71, by passing ammonia over anhydrous cobalt chloride, which is nearly colourless for many hours; the hexammine is first formed, and then, after several hours, the colour slowly changes to brown. The existence of this compound is not well established; it has been obtained twice, but both times from portions of the same specimen of cobalt chloride; other specimens of cobalt chloride did not give it. Analysis of the brown compound gave NH_3 0·5661, Co 0·1966, Cl 0·2358; $Co(NH_3)_{10}Cl$ requires NH_3 0·5673, Co 0·1964, Cl 0·2362. The vapour-pressure curve lies very much above that of the hexammine, and, on keeping, it loses its colour and passes into the hexammine. The preparation of the compound is probably dependent on the amount of moisture present in the anhydrous chloride. The effect of heat on certain ammine derivatives of cobalt has also been investigated. In the case of hexamminecobaltic chloride, an evolution of ammonia commenced at 173°, and at 181° ammonium chloride sublimed, with the formation of chloropentamminecobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$; on raising the temperature to 260°, the decomposition is represented by the equation $6[CoCl_3,6NH_3] \longrightarrow 6CoCl_2 + 6NH_4Cl + N_2 + 28NH_3$. With mononitropentamminecobaltic chloride, a notable gas pressure was observed at 100°, whilst at 210° rapid evolution of gas took place. The gas liberated below 248° consisted of 70·3 c.c. nitrogen and 16·8 c.c. ammonia. The decomposition is represented by $[Co(NH_3)_5(NO_2)]Cl_2 \longrightarrow NH_3 + 2NH_4Cl + NH_4{\cdot}NO_2 + CoN$; $NH_4{\cdot}NO_2 \longrightarrow N_2 + 2H_2O$; $2CoN + 3H_2O \longrightarrow Co_2O_3 + 3NH_3$. In the case of trinitrotriamminecobalt, slight evolution of gas commences at 158°, but at 164° decomposition takes place with almost explosive violence, forming nitrogen, water, and cobaltic oxide, according to the equations

$$2[Co(NH_3)_3(NO_2)_3] \longrightarrow 2CoN + 2HNO_2 + 4NH_4{\cdot}NO_2;$$
$$4NH_4{\cdot}NO_2 \longrightarrow 4N_2 + 8H_2O;\quad 2CoN + 2HNO_2 \longrightarrow Co_2O_3 + H_2O + 2N_2.$$

J. F. S.

Physical Properties of Nickel. P. D. MERICA (*Chem. Met. Eng.*, 1921, **24**, 73—76).—A compilation of the most trustworthy results obtained for the thermal, electrical, magnetic, mechanical, and optical properties of pure and commercial qualities of nickel. A. R. P.

The Hexabasic Polymolybdates. S. POSTERNAK (*Compt. rend.*, 1920, **171**, 1213—1215. Compare this vol., ii, 51).—When increasing quantities of hydrochloric acid are added to a saturated solution of hexammonium heptamolybdate, a series of hexabasic polymolybdates having the general formula

$$(NH_4O)_3MoO(O{\cdot}MoO_2)_mO{\cdot}MoO(ONH_4)_3 + nH_2O$$

are obtained. Of these, the following have been prepared: the *nonamolybdate*, the *undecamolybdate*, the *dodecamolybdate*, *hydroxypentammonium tridecamolybdate*, *dihydroxytetrammonium tridecamolybdate*, and *trihydroxytriammonium tridecamolybdate*, $(NH_4O)_3MoO(O{\cdot}MoO_2)_{11}O{\cdot}MoO(OH)_3,19H_2O$. All these polymolybdates are transformed by an excess of alkali into orthomolybdates, for which the author suggests the constitution of hexabasic trimolybdates, $(RO)_3MoO{\cdot}O{\cdot}MoO_2{\cdot}O{\cdot}MoO(OR)_3 + nH_2O$.

W. G.

The Tetrabasic Polymolybdates. S. POSTERNAK (*Compt. rend.*, 1921, **172**, 114—117. Compare this vol., ii, 51, and preceding abstract).—If 25 c.c. of $2N$-sulphuric acid and 10 grams of ammonium sulphate are added to 100 c.c. of a 10% solution of ammonium molybdate, ammonium trihydrogen tetramolybdate, $NH_4O{\cdot}(OH)_2MoO(O{\cdot}MoO_2)_3{\cdot}OH,5H_2O$, described by Rosenheim as an octamolybdate (A., 1897, ii, 497), is obtained. In a vacuum over sulphuric acid, this salt loses its $5H_2O$, and a further molecule of water at 130—160°. Its aqueous solution when warmed at 40° gives needle-shaped crystals of ammonium trihydrogen pentamolybdate, $NH_4O{\cdot}(OH)_2MoO(O{\cdot}MoO_2)_4{\cdot}OH$, described by Rosenheim and Felix as a decamolybdate (A., 1913, ii, 224). If the tetramolybdate is recrystallised twice from water at 75°, the insoluble portion being filtered off, it gives triammonium trihydrogen tridecamolybdate, $(NH_4O)_3MoO(O{\cdot}MoO_2)_{11}O{\cdot}MoO(OH)_3,19H_2O$, the insoluble portion being ammonium trihydrogen hexamolybdate, $NH_4O{\cdot}(OH)_2MoO(O{\cdot}MoO_2)_5{\cdot}OH,H_2O$. All these tetrabasic polymolybdates, which contain, at the most, seven molybdic groups, arise from the decomposition of a more complex salt, which the author has separated by dialysis as *ammonium pentahydrogen tridecamolybdate*, $NH_4O{\cdot}(OH)_2MoO(O{\cdot}MoO_2)_{11}O{\cdot}MoO(OH)_3$.

The condensation of molybdic acid thus reaches its limit by the formation of tridecamolybdic acid. The current classification into ortho-, meta-, and para-molybdates is unsatisfactory. There only exist two groups of molybdates: (1) the hexabasic polymolybdates, of which the ortho- and para-molybdates are only particular cases; (2) the tetrabasic polymolybdates, which arise from the former by hydrolytic rupture of their chain. W. G.

Hydrolysis of Zirconyl Chloride and Sulphate at 0° and 20°. F. P. VENABLE and D. H. JACKSON (*J. Amer. Chem. Soc.*, 1920, **42**, 2531—2534).—The hydrolysis of $0{\cdot}2M$-, $0{\cdot}1M$-, and $0{\cdot}01M$-solutions of zirconyl chloride and zirconyl sulphate has been followed by the change in the relative conductivity with time at 0° and 20°. The conductivity increases slowly for three to four hours, at which point the experiments were interrupted. There appears to be in all cases an initial temperature adjustment on dissolving the salts, which is more noticeable at the higher temperature. A further set of experiments were carried out with zirconyl

chloride at the same temperatures and concentrations, in which 25-c.c. portions of the solution were withdrawn from time to time, and the ratio ZrO_4/IO_3 determined by titrating with iodic acid. Here also the temperature adjustment is to be observed. The precipitates obtained with iodic acid indicate the probable existence of the basic iodates $3ZrO(OH)_2,4ZrO(IO_3)_2$, $2ZrO(OH)_2,ZrO(IO_3)_2$, $ZrO(OH)_2,2ZrO(IO_3)_2$, and $3ZrO(OH)_2,2ZrO(IO_3)_2$. These compounds are obtained by washing the precipitates with either hot or cold water. J. F. S.

Revision of the Atomic Weight of Bismuth. A. CLASSEN and O. NEY (*Ber.*, 1920, **53**, [*B*], 2267—2270).—Magnesium phenyl bromide is treated with an excess of bismuth bromide (redistilled; in some cases made from pure metal) in ethereal solution, and the product is decomposed by ice-water and distilled in a current of steam. The residual non-volatile *bismuth triphenyl*, $BiPh_3$, m. p. 77·6°, is purified by crystallisation from absolute alcohol, and distillation (b. p. 242°/14 mm., 208°/0·07 mm.), and for the purpose of atomic-weight determination is left for ten hours over phosphoric oxide in a cathode-ray vacuum before weighing. Transference into bismuth oxide is effected by mixing weighed portions with pure oxalic acid in a porcelain crucible, moistening with pure alcohol, heating in an electric quartz muffle furnace at 250° (twenty hours), 250—400° (five hours), then 750°, and finally igniting in a stream of oxygen. From ten values of the ratio $2BiPh_3:Bi_2O_3$, the atomic weight of bismuth is obtained as 208·920 (lowest), 209·072 (highest), and in mean, Bi = 208·9967, a value which agrees with Hönigschmid and Birckenbach's recent determination (A., 1920, ii, 549). J. C. W.

Mineralogical Chemistry.

The Chemistry of the Earth's Crust. HENRY S. WASHINGTON (*J. Franklin Inst.*, 1920, **190**, 757—815).—The chemical composition of the materials of the earth is discussed. Elements are divided into two groups: (1) petrogenic elements, characteristic of igneous rocks, and of low atomic weight; (2) metallogenic elements, rare or absent in igneous rocks, but occurring in ores of high atomic weight. Beneath the silicate crust it is suggested that there is a zone essentially of nickel–iron, and below this a central core of metallogenic elements. The average densities of the continents, ocean floor, and various smaller regions of the earth appear to be inversely as their elevations. J. R. P.

Classification of the Sulpho-salt Minerals. EDGAR T. WHERRY and WILLIAM F. FOSHAG (*J. Washington Acad. Sci.*, 1921, **11**, 1—8).—The scheme previously outlined (A., 1920, ii, 764) is carried on for this group. The main divisions are based on the ratios of acid to basic sulphides, and the groups on the crystalline form. Minerals containing both univalent and bivalent metals are regarded as double compounds rather than as isomorphous mixtures. The sulpharsenate–sulphantimonate division is discarded, enargite, for example, being placed in the enargite (orthorhombic) group of the 5 : 1 division, and the formula written as $Cu_2S,4CuS,As_2S_3=Cu_3AsS_4$. L. J. S.

Secondary Sulphide Ore Enrichment: Copper Sulphides and Hydrogen Sulphide. S. W. YOUNG and NEIL PRESTON MOORE (*Econ. Geol.*, 1916, **11**, 349—365).—Fragments of massive chalcocite, chalcopyrite, bornite, or covellite were kept in sealed tubes for several weeks at 30° with liquid hydrogen sulphide and water or sulphuric acid (*N*/10), or potassium sulphide (10*N*—*N*/10-solutions). The acid and strongly alkaline solutions had little action, the greatest changes being effected by the neutral solution. "Blue" chalcocite gives a brown, colloidal solution, which flocculates and deposits a sooty coating on the fragment; this coating afterwards crystallises as small, six-sided plates of chalcocite. Iron (2%), present as an impurity in the original material, gave rise to chalcopyrite. Bornite breaks down into crystallised chalcopyrite, chalcocite, and covellite. "White" ("pseudo-hexagonal") chalcocite, chalcopyrite, and covellite are only slightly attacked. L. J. S.

Sulphide Ore Enrichment: Formation of Chalcopyrite. S. W. YOUNG and NEIL PRESTON MOORE (*Econ. Geol.*, 1916, **11**, 574—581).—Chalcocite and covellite were kept in sealed tubes for several weeks at 30° with liquid hydrogen sulphide, water, and an iron compound (ferrous sulphate, ferrous sulphide, or magnetite). A crust of pyrrhotite crystals was formed at the junction of the solution and the liquid hydrogen sulphide. Chalcocite gives rise to the formation of chalcopyrite, but covellite is only slightly attacked. When the chalcocite and magnetite are in actual contact, the action is much more intense. Bornite (Cu_5FeS_4) is probably a molecular compound of $CuFeS_2$ (chalcopyrite) and $2Cu_2S$ (chalcocite), and chalcopyrite is perhaps Cu_2S,FeS,FeS_2.
L. J. S.

A Crystalline Normal Dolomite from the Kneifelspitze, Berchtesgaden, Bavaria. EMANUEL GLATZEL (*Centr. Min.*, 1919, 289—293).—The dolomite is found in the form of rock-fragments of varying size, distinguished from the surrounding, pale yellow limestone by their white colour. The fragments are much weathered, and show on the surface a fine-grained, crystalline, sugar-like structure. The dolomite has D 2·792, contains only a

trace of hygroscopic water, dissolves practically completely in hydrochloric acid, and corresponds in composition with normal dolomite, $CaCO_3,MgCO_3$. E. H. R.

Orthoclases containing Barium. G. TSCHERMAK (*Tsch. Min. Mitt.*, 1914, **32**, 543—544).—Analysis I, by R. ZSIGMONDY, is of twinned crystals, D 2·575, of sanidine, from Samothrace Island, Ægean Sea; II, by E. Kolisko, of pure, water-clear adularia, from the St. Gothard district:

	SiO_2.	Al_2O_3.	Fe_2O_3.	BaO.	K_2O.	Na_2O.	Total.
I.	64·76	19·61	0·46	1·17	9·75	3·32	99·07
II.	64·47	19·29	—	0·78	14·11	1·43	100·08

L. J. S.

Composition of Aluminous Augites. G. TSCHERMAK (*Tsch. Min. Mitt.*, 1914, **32**, 520—534).—A discussion of recent analyses in the light of the theory [mixing of the molecules $Ca(Mg,Fe)Si_2O_6$ and $MgAl_2SiO_6$] proposed by the author in 1871, and a criticism of Boeke's work (A., 1914, ii, 283). Although the compound $MgAl_2SiO_6$ has not been prepared artificially, its existence is probable. The corresponding calcium compound, $CaAl_2SiO_6$, and $Mg_2Si_2O_6$ (clinoenstatite), are also assumed to be present to explain certain analyses. L. J. S.

Analysis of Rumpfite. G. TSCHERMAK (*Tsch. Min. Mitt.*, 1914, **32**, 542—543).—Material from the original locality in Styria is compact to fine grained, with pale yellowish-green colour, and often encloses small crystals of dolomite. Detached scales are optically positive with weak birefringence and variable axial angle, the optic axial plane being parallel to a side of the hexagonal outline. These optical characters are those of clinochlore, and the following analysis, by T. PANZER, agrees closely with that of typical clinochlore from Achmatovsk. Material dried at 100° contains 12·39% H_2O. The alkalis and slight excess of silica are referred to intermixed mica:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
31·31	20·07	0·82	1·36	33·30	0·85	0·39	12·87	100·97

L. J. S.

A Diopside containing Manganese from the Radautal near Harzburg. J. UHLIG (*Jahrb. Min.*, 1914, *Beil. Bd.*, **39**, 446—449).—Analysis of the mineral gave the following result:

SiO_2.	TiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.	Loss on ignition.	Total.
51·92	0·31	2·54	6·16	1·08	12·49	24·76	0·44	99·70

The mineral is to be regarded as a diopside rather than a pyroxene. It contains too little manganese to be classed as a "schefferite." It occurs embedded in prehnite in growths 0·1 mm. thick and 0·5—0·75 mm. long or in tiny, pale red veins of much smaller dimensions. It has D 3·30—3·33, mean refractive index 1·68. E. H. R.

Anthophyllite from Moravia. KARL SCHIRMEISEN (*Tsch. Min. Mitt.*, 1914, **32**, 512—519).—At Podoli, near Bobrau, granite is intrusive into a bronzite-bearing serpentine, and it contains embedded blocks and nodules of the serpentine. At the contact between the two rocks, and also surrounding the embedded blocks of serpentine, is a zone, 1—1·5 cm. thick, of fibrous anthophyllite, the fibres of which are arranged perpendicularly to the contact. Some biotite and actinolite are also present. The anthophyllite is almost colourless; it is orthorhombic and optically positive, with wide axial angle, D 3·0. Analysis by M. KREBS gave:

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Alkalis.	H_2O.	Ign.	Total.
56·34	2·33	9·76	2·05	0·80	23·39	0·60	1·13	1·64	98·04

These minerals are clearly of contact-metamorphic origin; the anthophyllite and actinolite were evidently formed by the addition of silica from the granite magma to the olivine of the peridotite, whilst the biotite may have arisen by the addition of magnesium silicate from the peridotite to the muscovite of the granite.

L. J. S.

Enclosures in Styrian Basalt-tuffs. JOS. SCHADLER (*Tsch. Min. Mitt.*, 1914, **32**, 485—507)—Basalt-tuffs containing blocks ("bombs") of various rocks foreign to the basalt occur at several places in southern Styria. The olivine-bombs (bulk analysis I) agree closely in composition with lherzolite, and contain olivine, 50·8; bronzite, 28·4; chrome-diopside, 13·8; picotite, 6·4; H_2O, 0·4%. Dilute hydrochloric acid dissolves the olivine portion, the silica of which also goes into solution; analyses are given of the soluble (II) and insoluble portions. When exposed to the weather, these olivine-bombs become coated with a green, earthy crust (anal. III), due to the alteration of the olivine to a mixture of minerals (differing apparently from serpentine). Analyses are also given of the soluble (IV) and insoluble portions; in this case very little silica goes into solution, but potassium hydroxide solution extracts 3·32% of free silica:

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I.	43·01	3·01	0·28	3·62	5·89	2·92	38·54	0·94	99·83*
II.	29·10	0·12	—	7·01	—	—	26·62	0·38	53·25
III.	47·37	2·50	0·89	8·66	2·88	3·07	22·71	9·14	99·72†
IV.	0·68	0·06	—	9·09	—	0·91	12·06	9·20	31·67
V.	40·72	nil	—	—	9·47	nil	49·88	—	100·07
VI.	53·40	3·66	0·34	4·66	4·04	0·75	33·16	0·26	100·27
VII.	49·87	5·44	1·76	2·95	2·50	20·74	16·26	0·55	99·87
VIII.	39·66	14·27	—	5·07	5·10	10·78	14·56	0·49	100·06‡
IX.	47·99	9·36	—	2·48	3·56	19·97	14·87	0·59	100·59§

* Incl. insoluble 1·62. † Incl. insoluble 2·50.
‡ Incl. TiO_2 4·60, MnO trace, K_2O 2·10, Na_2O 3·52. § Incl. TiO_2 1·25.

The pale yellow, transparent olivine gave V, D 3·351, corresponding with $Fe_2SiO_4 : Mg_2SiO_4 = 1 : 9·35$. The powdered mineral lost 0·35% at 150° and gained 1·05 at a red-heat, corresponding with the conversion of the whole of the ferrous oxide into ferric oxide. The

brown bronzite gave VI, D 3·318, corresponding with $(Mg,Fe)SiO_3$, 70·51; $(Mg,Fe)(Al,Fe,Cr)_2SiO_6$, 23·38; $(Mg,Fe)CaSi_2O_6$, 6·11 mol %. The leek-green chrome–diopside gave VII, D 3·337, corresponding with $(Mg,Fe)CaSi_2O_6$, 85·71; $(Mg,Fe)(Al,Fe,Cr)_2,SiO_6$, 14·29 mol. %.

Other bombs consist of hornblende and augite, either alone or with biotite and olivine. The black basaltic hornblende gave VIII, D 3·266; this composition is discussed; it agrees with Penfield's formula (A., 1907, ii, 102) only when the large amount of titanium is reckoned as Ti_2O_3. The augite (IX) is pale greyish-green in thin section, D 3·323; here the titanium is reckoned as TiO_2 to obtain a metasilicate formula. L. J. S.

Analytical Chemistry.

Weighing of the Precipitation Vessel with the Precipitate in Quantitative Micro analyses. Two Methods based on this Principle. Erich Gartner (*Monatsh.*, 1920, **41**, 477—498).—Two methods are described which permit of the estimation of precipitates weighing 2—15 mg. with sufficient accuracy, the only requisites being a Kuhlmann microchemical balance and such simple apparatus as is easily constructed. In each case the whole of the operations are carried out in a single vessel, this being either an asbestos filter-tube or a pointed centrifuge-tube. A tare of slightly less (1—2 mg.) weight than the vessel is prepared, the three necessary weighings then requiring only the tare, a 1 cg. weight, and the rider. Adhesion of the precipitate to the wall of the vessel causes no error, and both procedures are found to give accurate results.

T. H. P.

The Importance of Adsorption in Analytical Chemistry. III. The Adsorption of Acid by Filter Paper. I. M. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 1571—1577).—Filter paper cut into pieces of about 0·5 cm.^{2} surface were kept in an atmosphere saturated with water-vapour until no further increase of weight took place. Weighed quantities were then gently shaken with dilute acid solutions of known strength, and after equilibrium was reached, aliquot quantities were drawn off and titrated. The first paper employed gave results conforming to the adsorption equation $X/m = ac^{1/n}$, where X/m is the number of milli-mols. taken up by 1 gram of the paper, c is the end concentration of the acid, and a and $1/n$ are constants. By titrating the anion, it was found that only hydrion was adsorbed. The results held only for very low concentrations of acid, and were found to apply to hydro-

chloric, nitric, sulphuric, and oxalic acids, the constants being the same for all these.

The work could not be completed, as no further supplies of the particular paper used could be obtained. Other standard filter papers were then examined, and it was found in all cases that the amount of acid adsorbed was constant, and was exactly equivalent to the alkalinity of the ash. Cotton-wool in which the ash had been reduced to a minimum by treatment with hydrofluoric acid was found to adsorb scarcely at all. The taking-up of acids by filter paper, therefore, appears to be entirely a chemical action.

S. I. L.

Action of Surface Adhesion in Ring Reactions. F. REISS (*Zeitsch. öffentl. Chem.*, 1920, **26**, 281—283. Compare A., 1919, ii, 166).—The author and G. Diesselhorst have shown (*loc. cit.*) that the greater the surface of contact between two layers of liquid, the more sensitive is the reaction in such cases as the diphenylamine reaction for nitrates; this increase in surface may be attained by carrying out the reactions in test-tubes containing colourless glass beads.

W. P. S.

Normalities of Standard Solutions. YUKICHI OSAKA (*Mem. Coll. Sci. Kyōtō* 1920, **4**, 113—125).—See A., 1920, ii, 187, under the title, "Influence of Temperature on the Strength of Standard Solutions in Quantitative Analysis."

The New Indicator. R. W. KINKEAD (*Chem. News*, 1921, **122**, 4—5).—By the action of ethyl nitrate on magnesium phenyl bromide a deep blue solution was obtained, which had the properties of an indicator, turning pink with acids and blue with alkalis.

J. R. P.

Volumetric Estimation of Mixtures of Acids and of Bases, and of Polybasic Acids or Bases. HENRY THOMAS TIZARD and ALFRED REGINALD BOEREE (T., 1921, **119**, 132—142).

The Application of Conductivity Titrations in Analysis. I. M. KOLTHOFF (*Chem. Weekblad*, 1920, **17**, 694—701).—The conductivity-titration of a strong acid with a strong base, and vice versâ, is of importance where very dilute or coloured solutions must be examined. With weaker acids and bases, the straight lines which make the determination so accurate in the first case are not obtained. The curves obtained may be regarded as resulting from the superposition of two lines, one the conductivity of the dissociated fraction of the acid or base, the other the conductivity of the neutral salt formed; the latter line starts at the origin, and meets both the actual conductivity curve determined by measurement and the curve resulting from addition of excess of reagent, and by plotting it independently, the end-point can be accurately found in all cases. In the case of a weak acid being titrated with sodium hydroxide, for example, the determination is carried out in the usual

way. A "salt line" is then obtained by adding to a volume of water equal to the volume of the dilute acid solution used, increasing quantities of the sodium salt of the acid, in solution of equivalent concentration to the sodium hydroxide solution used, and at the same temperature. This salt line is plotted on the same diagram, and intersects the line given by the titration at the neutralisation point.

For very weak acids and bases, good results can be obtained only if the concentration and the dissociation constants are within certain limits; thus phenol, boric acid, hydrocyanic acid, and others which have a dissociation constant in $N/10$-solution not less than 10^{-10} (or for $N/100$-solutions not less than 10^{-9}) can be accurately determined. For bases, the minimum dissociation constant in $N/10$-solutions is $1{\cdot}6 \times 10^{-10}$; thus hexamethylenetetramine can readily be titrated in $N/10$- or $N/100$-solution with N-hydrochloric acid, as can also aniline and many of its derivatives, alkaloids, etc. A weak acid can be accurately titrated with a weak base, and vice versâ, if the dissociation constants are not less than 3×10^{-6}, the dilutions here being unimportant.

The same principles may be applied to the titration of a weak acid in presence of one either much stronger or much weaker, provided that the dissociation constants fall within the necessary limits. Where these limits are exceeded, the salt line may be plotted, or resort may be had to addition of alcohol, by means of which the dissociation constants of most organic acids are greatly reduced. The case of polybasic acids, and the displacement of a weak acid or base by a stronger one, can also be satisfactorily dealt with if the dissociation constants are not too close to one another.

S. I. L.

Catalysis of Permanganate Titrations. Paul H. Segnitz (*J. Ind. Eng. Chem.*, 1920, **12**, 1196—1197).—The addition of a small quantity of manganese sulphate solution considerably increases the rate of reaction between permanganate and hydrogen peroxide or sodium oxalate; the use of the catalyst does not affect the end-point of the titration.

W. P. S.

Apparatus for Gas Analysis by Absorption and Titration. R. S. Tour (*Chem. Met. Eng.*, 1920, **23**, 1104—1106).—For determining the volume of residual gas, after absorption of one constituent of a gas by a suitable reagent, a gas-volume compensometer may be used. The apparatus comprises a gas-flask which can be connected at one end by means of a two-way tap either to the absorber or to one limb of a manometer, the other limb of which is expanded into a compensometer and is completely enclosed by the gas flask. The other end of the flask is connected with a reservoir, and two marks on the flask serve to indicate a zero and a convenient volume for displacement. After the flask has been filled with water, communication is established with the absorbing vessel, and the residual gas is drawn in by discharging a certain quantity of water. The flask is then connected with the manometer, and the correction

factor, or the corrected volume at 760 mm., 0°, dry, is read off on the scale. The amount of the absorbed constituent in the original gas is calculated from $100 - Y/Y = VJ/22 \cdot 4NQ$, where Y = the percentage of constituent, V = vol. in c.c. of residual gas, corrected to standard conditions, J = valency of absorbed constituent, N = normality of reagent, Q = c.c. of reagent used for titration. The apparatus gives an accuracy of $\pm 0.5\%$. The use of a nomograph facilitates the graphical solution of the above equation. The methods of calibrating the apparatus to determine the compensometer constant and of graduating the manometric scale are described. W. J. W.

Estimation of Chlorides in Blood. A. S. WETMORE (*J. Biol. Chem.*, 1920, **45**, 113—118).—The sample of blood is collected in dry potassium oxalate, and the proteins removed by a precipitation of cupric hydroxide. An addition of calcium hydroxide powder to the filtrate is then made to remove the oxalate and most of the phosphate. After filtration, the chlorides are precipitated by adding an excess of standard silver nitrate solution, and the estimation made by titrating the excess with potassium thiocyanate. J. C. D.

The Microchemical Reactions of Iodic Acid. G. DENIGÈS (*Compt. rend.*, 1921, **172**, 62—63. Compare A., 1920, ii, 388, 555, 706, 751; *Bull. Soc. Pharm. Bordeaux*, 1920, **211**).—A claim for priority over Bolland (this vol., ii, 57). W. G.

Analysis of Mineral Sulphide Water. J. G. FAIRCHILD (*J. Washington Acad. Sci.*, 1920, **10**, 559—565).—The alkalinity of a water-containing alkali and alkaline earth hydrosulphides and hydrogen carbonates increases continuously with the escape of hydrogen sulphide or with the precipitation of sulphur. The acidity of calcium and magnesium chlorides towards the alkali sulphides is pronounced, but has less effect on the hydrogen carbonates. Although the addition of a small quantity of barium chloride solution to an ordinary carbonate water aids in the decomposition of the hydrogen carbonate ions, it has no such effect if the water contains a considerable quantity of alkali sulphides. A method proposed for the estimation of the carbon dioxide present as hydrogen carbonate and of volatile hydrogen sulphide consists in boiling a quantity of the water for five minutes in a rapid current of pure hydrogen, and absorbing the carbon dioxide and hydrogen sulphide in an ammoniacal solution containing cadmium chloride and barium chloride. This solution is then acidified with acetic acid, and the liberated carbon dioxide is collected; the hydrogen sulphide remains fixed as cadmium sulphide. W. P. S.

Water Analysis. V. [Estimation of Sulphuric Acid.] L. W. WINKLER (*Zeitsch. angew. Chem.*, 1920, **33**, 311—312. Compare A., 1915, ii, 173; 1916, ii, 194, 448; 1917, ii, 501).—An approximate estimation of sulphuric acid in potable waters

is obtained by observing the time taken by the clear liquid to develop the first signs of cloudiness when to 5 c.c. of the sample, acidified with 2·5 c.c. of 10% hydrochloric acid, 2·5 c.c. of 10% barium chloride solution are added. The test is conveniently carried out beside a blank in two test-glasses standing on a black surface to facilitate observation, and the mg. of SO_3 per litre corresponding with the time are obtained either from the table given, or, preferably, by actual tests on dilute sulphuric acid solutions of known strength. The upper and lower limits of concentration for the purpose of this test are about 100 mg. and 10 mg. of SO_3 per litre, the corresponding times being five seconds and five minutes respectively, and the limits of error may be within 5 mg. at the lower concentrations and 10 mg. at the higher concentrations. For a gravimetric estimation of sulphates, it is generally necessary to concentrate by evaporation unless large quantities are present, but inaccurate results are obtained unless calcium is first removed by precipitation with 0·5—1·0 gram of sodium hydroxide and 1—2 grams of sodium carbonate per litre, the precipitate being allowed to settle, and 1000 c.c. of the supernatant, clear liquid evaporated to dryness after acidification with hydrochloric acid. The residue is then dissolved in 25 c.c. of water, filtered from silicic acid, and the sulphuric acid estimated as previously described (A., 1920, ii, 504). G. F. M.

The Use of Permanganate in the Kjeldahl Method modified for Nitrates. I. K. PHELPS (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 69—71).—In the estimation of nitrates by the modified Kjeldahl process with a sulphuric acid–salicylic acid mixture, the addition of potassium permanganate at the end of the boiling may cause the loss of nitrogen, and it should therefore be omitted. W. G.

Investigation of the Kjeldahl Method for Estimating Nitrogen. I. K. PHELPS and H. W. DAUDT (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 72—76).—For the digestion in open flasks, 25 c.c. of sulphuric acid and 10 grams of potassium sulphate, or 8·2 grams of sodium sulphate, may be used without loss of ammonia. If the amount of acid is reduced to 15 c.c., the loss of ammonia is very small, but if the amounts of sulphates used are appreciably increased, losses of ammonia occur. The hydrolysis of refractory substances like pyridine zinc chloride is complete if the substance (0·4 gram) is boiled for two and a-half hours with a mixture of 0·7 gram of mercuric oxide, 10 grams of potassium sulphate, and 25 c.c. of acid in an open flask.

The influence of the reagents and the apparatus on the accuracy of the modified Kjeldahl process is indicated, and in routine work the results should be controlled by blank experiments. W. G.

Influence of Potassium Permanganate on Kjeldahl Nitrogen Estimations. DONALD C. COCHRANE (*J. Ind. Eng. Chem.*, 1920, **12**, 1195—1196).—Comparative estimations of

nitrogen in feeding stuffs and fæces by the Kjeldahl method, with and without the addition of permanganate, showed that uniformly higher results were obtained when permanganate was used, provided that the latter was added about ten seconds after the acid digestion mixture ceased to boil. W. P. S.

Micro-estimation of Nitrogen in Agricultural Materials. W. GEILMANN (*J. Landw.*, 1920, **68**, 235—249).—A description of a micro-method for the estimation of nitrogen in proteins, ammonium salts, etc., using only a few mg. for the estimation; the method consists essentially in a micro-Kjeldahl digestion, followed by the liberation of the ammonia formed either by steam distillation or by aspiration with a current of air after the mixture has been rendered alkaline. The ammonia is absorbed in $N/70$-acid, and the excess of this is titrated with $N/70$-alkali solution, using methyl-red as indicator. W. P. S.

Gasometric Estimation of Nitrogen and its Application to the Estimation of the Non-Protein Nitrogen of Blood. R. L. STEHLE (*J. Biol. Chem.*, 1920, **45**, 223—228).—The first step is to treat the substance by the usual Kjeldahl digestion, after which decomposition with sodium hypobromite is carried out. The method is stated to possess certain advantages over the usual Kjeldahl method. J. C. D.

Iodometric Estimation of Amino-Nitrogen in Organic Substances. H. H. WILLARD and W. E. CAKE (*J. Amer. Chem. Soc.*, 1920, **42**, 2646—2650).—The Kjeldahl method of estimating nitrogen can be hastened by adding solid potassium persulphate to the cold, charred solution of organic matter in concentrated sulphuric acid. Water must be excluded, otherwise some oxidation of ammonia occurs. The mixture is warmed carefully for about one minute until colourless, and then boiled to decompose excess of persulphate. The solution may now be cooled, diluted, rendered just alkaline, and the ammonia titrated by means of standard sodium hypobromite solution (compare Artmann and Skrabal, A., 1907, ii, 196). J. C. W.

Estimation of Nitrogen Oxides in Gases. G. B. TAYLOR (*Chem. Met. Eng.*, 1920, **23**, 1112).—A 2-litre bottle is filled with the gas to be examined, oxygen being passed in if not present in sufficient quantity to convert nitric oxide into peroxide, and the pressure and temperature are recorded. Twenty-five to fifty c.c. of 1·5% hydrogen peroxide solution, prepared by diluting the commercial 3% peroxide with an equal volume of water and neutralising with $N/10$-sodium hydroxide, are then added, and the mixture is shaken until the red colour of the gas disappears. After five minutes, the bottle is again shaken, and the solution is then titrated with $N/10$-sodium hydroxide, with methyl-orange as indicator. Percentage nitric oxide=

$$224a/\{v(b-p/760)(273/273+t)\},$$

where a=c.c. of $N/10$-sodium hydroxide, v=volume of the bottle in c.c., b=barometric pressure, p=pressure in the bottle before sampling, and t=temperature of gas. The formula is correct for nitric oxide concentrations up to 3%, where volume change, due to formation of nitrogen peroxide, may be neglected. If the temperature of the gas is much higher than normal temperature, a measured volume of water is added after the hydrogen peroxide. Then percentage nitric oxide=

$$224a/\{(v-v')(b-p-w/760)(273/273+t)+2\cdot24a\},$$

where w=vapour pressure of water at t° and v'=volume of peroxide plus water. W. J. W.

Removal of Nitrates by means of Alcohol. R. SCHNEIDEWIND (*Chem. Met. Eng.*, 1921, **24**, 22).—In analytical processes which require the absence of nitric acid or nitrates their removal may be more conveniently effected by means of ethyl alcohol than by the usual method of boiling down with sulphuric acid. For example, to a solution containing 20 c.c. of nitric acid and 150 c.c. of water, 15 c.c. of sulphuric acid are added, and when nearly boiling 5 c.c. of ethyl alcohol are carefully run in from time to time, until further addition no longer causes an evolution of nitrous fumes. The boiling is then continued to expel the excess of alcohol, and the resulting solution is sufficiently free from nitric acid to give no brown ring test, and not to oxidise hydrogen sulphide. G. F. M.

Volatilisation Losses of Phosphorus during Evaporations of Phosphates with Sulphuric Acid or Fusions with Pyrosulphate. W. F. HILLEBRAND and G. E. F. LUNDELL (*J. Amer. Chem. Soc.*, 1920, **42**, 2609—2615).—No volatilisation losses of phosphorus occur during evaporations of sulphuric acid solutions of phosphates, provided the evaporations are carried on at temperatures below 150° and stopped when fumes appear. Such evaporations are best performed over radiators. Volatilisation losses during evaporation of sulphuric acid solutions of phosphates are occasioned by (i) evaporation to complete expulsion of sulphuric acid, (ii) evaporation at high temperatures, such as 200—260°, and (iii) unduly prolonged evaporation at temperatures above 150°. Evaporations involving only a drop or two of sulphuric acid, such as apply in silica treatments, do not cause measurable losses. Fusions with pyrosulphate in covered crucibles and at a dull red heat result in appreciable losses in the case of secondary phosphates, and may result in slight losses in the case of basic phosphates. Orthophosphoric acid and primary and secondary orthophosphates suffer conversion to pyro- and meta-phosphoric acid or phosphates when evaporated to dryness with sulphuric acid or fused with pyrosulphate; such "converted" compounds must be subjected to re-conversion treatments before precipitation with molybdic acid or magnesia mixture. J. F. S.

General Method for the Detection and Estimation of Arsenic. ÉMILE KOHN-ABREST (*Compt. rend.*, 1920, **171**, 1179—1182).—The organic matter (animal organs, physiological fluids, or foodstuffs) is calcined with a mixture of magnesium oxide and magnesium nitrate, using 35 c.c. of a 20% solution of magnesium nitrate and 1 gram of magnesium oxide, the mixture being first dried at 110° (compare Gautier and Clausmann, A., 1917, ii, 421). After calcining, the residue is extracted with dilute sulphuric acid and the extract is transferred to a Marsh's apparatus for the estimation. As an alternative the ash is extracted with dilute hydrochloric acid, the extract being heated on a water-bath with potassium iodide, and the iodine liberated titrated with a standard thiosulphate solution. The liquid is then made alkaline with sodium hydrogen carbonate, and the arsenite present is titrated with standard iodine solution. The second titration gives a measure of the arsenic present. W. G.

Estimation of Arsenic in Neosalvarsan [Salvarsan, etc.]. A. KIRCHER and F. VON RUPPERT (*Ber. Deut. pharm. Ges.*, 1920, **30**, 419—421).—From 0·2 to 0·3 gram of salvarsan (or its derivatives) is boiled with 20 c.c. of sulphuric acid and 15 grams of potassium sulphate in a 500 c.c. round flask fitted with a tube preferably ground in at the neck, and bent downwards to terminate in a bulb absorption tube containing a little water. When all the organic matter has been destroyed, the absorption bulb and tube are rinsed out into the flask and the liquid is diluted to about 250 c.c., boiled for five minutes to expel sulphur dioxide, partly neutralised with sodium hydroxide, and dilute iodine solution added drop by drop in presence of starch to oxidise the last traces of sulphur dioxide. The solution is then decolorised with a few drops of thiosulphate, and after saturation with powdered sodium hydrogen carbonate, the arsenious oxide is titrated with $N/10$-iodine (1 c.c. = 0·003748 gram As). It is advisable to perform a blank experiment at the same time as a check on the purity of the reagents G. F. M.

[**Estimation of Arsenic Trihydride.**] H. THOMS and L. HESS (*Ber. Deut. pharm. Ges.*, 1920, **30**, 483—489).—See this vol., ii, 110.

Estimation of Arsenic and Phosphoric Acids in the Presence of Large Amounts of Salts. VI. Applications. L. DEBOURDEAUX (*Bull. Sci. Pharmacol.*, 1920, **27**, 424—435. Compare A., 1920, ii, 770).—*Estimation in the Presence of Alkali and Alkaline-earth Chlorides.*—When 3% or more of alkaline-earth chlorides are present, the solution is rendered neutral to phenolphthalein by cold sodium hydroxide solution (D 1·3), the precipitate is filtered, and washed with a solution of barium, strontium, or calcium nitrate (depending on which of these alkaline earths is present in the precipitate) (200 c.c. of a 5% solution, plus 6·5 c.c.,

7·5 c.c., or 5 c.c. respectively of sodium hydroxide solution [D 1·3], the whole being made to a litre with water). The precipitate is dissolved in nitric acid, occluded chlorides are precipitated by silver nitrate, and the phosphoric and arsenic acids in the filtrate are precipitated by an excess of silver nitrate, as described previously (*loc. cit.*). Errors of +0·03 to +0·30% are reported. When alkali chlorides are present in excess, the neutralised solution is treated with sufficient 5% barium nitrate solution to precipitate the arsenic and phosphoric acids as the tribasic salts, together with an excess equivalent to 15 grams of hydrated barium hydroxide per litre; sodium hydroxide (D 1·3), equivalent to one-thirtieth of the barium nitrate used, is also added. The precipitation is effected on a boiling-water bath during one hour. After being cooled, the precipitate is collected, washed with the barium nitrate solution described above, and the estimation completed as usual.

Estimation in the Presence of Ammonium Chloride.—The solution of sodium arsenate or phosphate containing ammonium chloride is treated on a water-bath with an excess of nitric acid, and then evaporated to dryness. The residue is dissolved in a little water and nitric acid, traces of sulphuric acid and hydrochloric acid are removed by barium nitrate and silver nitrate, and the arsenic or phosphoric acid in the filtrate is estimated as described, the error being +0·01 to +0·18%.

Estimation in the Presence of Mixtures of Sulphates and Alkali Chlorides.—Sulphuric acid (D 1·8) sufficient to liberate the chlorine as hydrochloric acid is added, and then as many c.c. of nitric acid (D 1·4) as are equal to one and a-half times the weight of the sulphuric acid used, the solution is evaporated to dryness, and then again with nitric acid to expel all the hydrochloric acid, and the estimation is made with the residue as described above.

Estimation in the Presence of Chromates.—Five % calcium nitrate solution is added sufficient to precipitate the arsenic or phosphoric acid as the tribasic salt, and an excess equivalent to saturation with calcium hydroxide; sodium hydroxide solution is then added equivalent to one-thirtieth of the calcium nitrate solution used. The mixture is diluted to 1500 c.c., heated on the water-bath for one hour, and filtered hot; the precipitate is washed with the alkaline calcium nitrate solution described above, returned to the precipitation flask, dissolved in 1200 c.c. of water and 20 c.c. of nitric acid, and reprecipitated by the alkaline calcium nitrate solution, this procedure being repeated until the precipitate is white and the mother liquor gives but a faint reaction of a chromate. The arsenic or phosphoric acid in the precipitate is then estimated as usual, with an error of +0·11 to +0·22%. CHEMICAL ABSTRACTS.

New Micro-combustion Furnace for Carbon, Hydrogen, and Nitrogen Estimations. W. DAUTWITZ (*Chem. Zeit.*, 1920, **44**, 963).—The apparatus, including absorption stands, is mounted on a board covered with "Eternite," and is movable as a whole. The combustion tube, which is of the dimensions recommended by

Pregl, is heated from the sides by gas jets from two parallel gas tubes situated on either side of and slightly below it. These tubes are supplied with gas from three Bunsen burners which are fixed to the board and so constructed as to support the furnace. The part of the combustion tube containing the packing rests on an asbestos trough, and is covered by a chamber with a slot at the top for the escape of furnace gases. The number of gas jets in use can be controlled at will by means of a special tap. The apparatus can be used for the estimation of nitrogen as well as for ordinary combustions. J. H. L.

An Aid in the Estimation of Silica. S. R. SCHOLES (*Chem. Analyst*, 1920, **29**, 22—23).—A small amount of methyl-orange is added to the acid liquid before evaporation. This serves as an indicator to ensure acidity, and dyes the gelatinous solid as it separates from the solution. Every particle becomes coloured, and is less likely to be lost. CHEMICAL ABSTRACTS.

Potassium Hydrogen Oxalate as a Standardiser in Alkalimetry. YÛKICHI ÔSAKA and KINJI ANDÔ (*J. Tokyo Chem. Soc.*, 1920, **41**, 945—951).—Potassium hydrogen oxalate is used conveniently as a standardiser in alkalimetry, and can be easily prepared by dissolving 86 grams of crystallised normal oxalate and 57 grams of oxalic acid in 500 grams of water. The solution is allowed to crystallise at 25—60° for forty-eight hours, the crystals filtered with the aid of suction, and washed three times with 50 c.c. of water at 50°. K. K.

Estimation of Potassium by the Lindo-Gladding Method. H. C. MOORE and R. D. CALDWELL (*J. Ind. Eng. Chem.*, 1920, **12**, 1188—1189).—In the presence of sodium salts, low results are obtained when the potassium platinichloride is washed with 80% alcohol, although potassium platinichloride is equally insoluble in 80% and 95% alcohol. The deficiency appears to be due to the solvent action of sodium salts in alcoholic solution, and not to the lower strength of the alcohol itself. W. P. S.

Analysis of Leucites and Leucitic Minerals. G. TOMMASI (*Ann. R. Staz. Agrar. sperim.*, 1917—1919, II, **9**, 95—106).—The author describes a method for the estimation of potassium in leucites and rich leucitic minerals, the mineral being first brought into solution by treatment with hydrochloric and nitric acids. [See also *J. Soc. Chem. Ind.*, 1921, February.] T. H. P.

The Estimation of Calcium in the Presence of Phosphates. J. F. BREAZEALE (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 124—134).—For the estimation of calcium in material, such as plant ash, if manganese is absent, the ash is dissolved in dilute hydrochloric acid, the solution boiled, and made slightly alkaline with ammonia. A saturated solution of oxalic acid is then added until the liquid is just acid. This acid will dissolve the phosphates

of iron and magnesium, and convert the calcium phosphate into calcium oxalate. The solution is again made alkaline with ammonia, and then just acid with oxalic acid. The calcium oxalate is collected in the usual way, and the calcium is estimated either gravimetrically or volumetrically. If manganese is present, it will be precipitated as oxalate along with the calcium oxalate. In this case, the precipitate, after being collected and washed, is dissolved in excess of hydrochloric acid, the solution is made alkaline with ammonia, and a little ammonium oxalate is added. The calcium is precipitated as oxalate, whilst the manganese remains in solution.

Calcium oxalate is not soluble in oxalic acid solution at the ordinary temperature, but is appreciably soluble in boiling 30% acid. It is not soluble in solutions of ammonium or sodium salts in the presence of oxalic acid, but it is markedly soluble in solutions of sodium nitrate, chloride, or sulphate alone at the ordinary temperature, and still more so in their boiling solutions. W. G.

Stabilisation and Standardisation of Thiosulphate Solution for the Copper Assay. A. H. Low (*Chem. Analyst*, 1920, **30**, 18—19).—The standard solution will keep almost indefinitely if stored in amber-glass bottles and treated with about 5 grams of sodium hydroxide per litre to neutralise any carbonic acid present. It is standardised against the ordinary permanganate solution (the iron value $\times$ 1·139 = the copper value). About 35 c.c. of the permanganate solution are added to 150 c.c. of water, 5 c.c. of glacial acetic acid, and 6 c.c. of 50% potassium iodide solution, the liberated iodine is titrated with the thiosulphate solution until the colour is faint, starch and 2 c.c. of silver nitrate solution (about 4 grams per litre) are added, and the titration is completed. The yellow colour of the silver iodide produced destroys the purple tinge of the mixture, and the delicacy of the end-point is thus enhanced.

This method of standardisation is rapid, and is recommended as being possibly more accurate than that based on the use of metallic copper. CHEMICAL ABSTRACTS.

Iodometric Estimation of Copper. PETER KLASON (*Svensk. Kem. Tidskrift*, 1919, **31**, 211—220).—The iodometric methods of estimating copper have been critically examined with the view of using one for the estimation of sugars after reduction by Fehling's solution. Moser's results are confirmed (A., 1905, ii, 64). Low's method is inaccurate, because (1) the nitrite, which is not completely removed, causes interference; (2) the acetic acid used is insufficient to decompose the complex copper compounds formed; and (3) the presence of ammonium acetate interferes with the titration. The following modification gives good results. The copper solution, containing hydrochloric acid and nitrite, is neutralised with concentrated ammonia until the colour has passed through yellow and brown to blue. The brown colour is restored by adding 2 c.c. of acetic acid, the volume of the solution is reduced

to 6 c.c. by boiling, 50% potassium iodide is added, and then water, so that the solution contains not less than 100 mg. of copper in 30 c.c., and the solution is then titrated with thiosulphate. In eight experiments, the largest difference between the volume of copper solution used and the titration is 0·08 c.c.

CHEMICAL ABSTRACTS.

Volumetric Estimation of Mercury. A. H. LOW (*Chem. Analyst*, 1920, **29**, 13—14).—The mercury is precipitated as the sulphide, the well-washed precipitate is rinsed with as little hot water as possible into a flask, boiled with 5—6 c.c. of concentrated sulphuric acid and not more than 0·5 gram of solid potassium permanganate until the mixture fumes strongly, the heating is discontinued, and solid oxalic acid is added slowly until the manganese dioxide has disappeared. The mixture is again heated until it fumes strongly, and diluted, after cooling, with about 100 c.c. of water. The solution, which should be quite clear, is treated with the ferric indicator and titrated with $N/10$-thiocyanate (1 c.c. = 0·01 gram of mercury). The method is satisfactory in the absence of chloride or bromide.

If the sulphide stain on the filter paper is worth recovery, the wet paper is warmed on a watch-glass with solid permanganate and dilute sulphuric acid (1 : 1), and the soluble mercury salt rinsed into the flask containing the balance of the sulphide. The filter paper should now be quite clean after treatment with oxalic and sulphuric acids.

CHEMICAL ABSTRACTS.

Estimation of Mercury in the Brain. HANS HÜSGEN (*Biochem. Zeitsch.*, 1920, **112**, 1—22).—See this vol., i, 145.

Detection of Manganese in Presence of Phosphates. TH. SABALITSCHKA and W. ERDMANN (*Ber. Deut. pharm. Ges.*, 1920, **30**, 443—445. Compare A., 1920, ii, 334, 389, 774, 775). —A further criticism of Schmidt's method (*loc. cit.*). In presence of an excess of barium phosphate, manganese is completely precipitated as phosphate by excess of ammonia, and in the further examination of the precipitate, after removal of the phosphoric acid, a flocculent precipitate of manganese oxalate is obtained with ammonium oxalate, which is very liable to be mistaken for calcium. In presence of calcium phosphate, some of the manganese is precipitated in a similar way by ammonia, whilst the rest remains in solution with the zinc in the normal fashion. It is further pointed out that only by leading hydrogen sulphide into the ammoniacal solution, and not by the simple addition of ammonium sulphide, is manganese precipitated entirely as sulphide from its solutions in presence of phosphates or oxalates.

G. F. M.

The Precipitation of Tin by Iron. N. BOUMAN (*Rec. trav. chim.*, 1920, **39**, 711—714. Compare A., 1920, ii, 547).—A reply to Kolthoff (A., 1920, ii, 763), in which the author presents certain new experiments in support of his views.

W. G.

Gravimetric Estimation of Bismuth as Phosphate and its Application to the Analysis of Ores. W. R. SCHOELLER and E. F. WATERHOUSE (*Analyst*, 1920, **45**, 435—439).—The cold nitric acid solution of the bismuth salt (which should be free from chloride) is treated with ammonia until a slight permanent precipitate is formed; 2 c.c. of concentrated nitric acid are then added, the mixture is boiled, and 10% diammonium phosphate solution is added slowly, about 60 c.c. of this solution being required for 0·4 to 0·5 gram of bismuth. The mixture is diluted with boiling water to 400 c.c., the precipitate collected after fifteen minutes, washed with hot 3% ammonium nitrate solution containing a few drops of nitric acid per litre, dried, and ignited at a low temperature. The weight of the precipitate is multiplied by 0·6965 to obtain the amount of bismuth. A process for the estimation of bismuth in ores is also described in detail; in this method, the bismuth is precipitated by treating the hydrochloric acid solution with iron wire; copper, arsenic, and antimony are removed subsequently by extracting the mixed sulphides with sodium cyanide and sulphide solution, and the bismuth is then converted into phosphate and weighed as such. W. P. S.

The Volumetric Estimation of the Methoxyl Group. J. TROEGER and E. TIEBE (*Arch. Pharm.*, 1920, **258**, 277—287).—The demethylation of cusparine by means of dry hydrogen chloride (Troeger and Müller, A., 1915, i, 447) is quantitative in respect both of the pyrocusparine and of the methyl chloride produced. Experiments have therefore been performed to ascertain how far this method may be generalised. The material (0·1 gram), in a boat, is placed in a tube surrounded by a mantle, fitted with an observation window and a thermometer. Air having been displaced by dry hydrogen chloride, the apparatus is heated until bubbles of gas are seen to be escaping from the substance. The methyl chloride so produced is collected in a nitrometer, most suitably over 30—35% sodium hydroxide solution, which only absorbs 0·3 c.c. of the gas per hour, as against 7·0 c.c. by water. In order to conserve the alkali, a T-piece is fitted between the decomposition tube and the nitrometer, through which the gas used to displace air is allowed to escape. It is unnecessary to correct for the vapour tension of water, but allowance must be made for absorption of the gas, as just indicated, and for the presence of air, which originates from the concentrated acid used to generate the hydrogen chloride. This is determined as the unabsorbed residue when the gas collected is transferred to a eudiometer over water. The results obtained with a number of alkaloids, whilst not absolutely accurate, gave a clear indication as to the number of methoxyl groups present, but with compounds, for example, anisic acid, which volatilise below the temperature necessary, the results are, naturally, valueless. Whilst the Zeisel method is not applicable to compounds containing sulphur, the present method gives an approximate value in the case of galipinesulphonic acid, although not in another instance. J. K.

Tables giving Alcoholic Strength from the Specific Gravity. II. From 25% to 50% of Ethyl Alcohol by Weight. G. TOMMASI (*Ann. R. Staz. Chim. Agrar. sperim.*, 1917—1919, II, **9**, 37—74).—The tables given show the percentages of ethyl alcohol by weight and by volume (at 15°), and the number of grams of alcohol in 100 c.c. at 15°, for the specific gravities of aqueous-alcoholic solutions determined at a number of different temperatures ranging from 10°/15° to 25°/15°.

T. H. P.

A Volumetric Method for Estimating several Sugars in the Presence of each other. TH. VON FELLENBERG (*Mitt. Lebensm. Hyg.*, 1920, **11**, 129—153).—A method applicable to the estimation of raw sugar, invert-sugar, dextrose, maltose, and lactose when three are present in the same solution is proposed. It is based on the action of a weak and a strong inversion and a decomposition with sodium hydroxide of the various sugars present, with subsequent reduction of a copper solution, followed by an iodometric titration of the cuprous oxide formed. For details of calculation and procedure the original must be consulted. Examples of its application to infant foods, fondant filling, commercial glucose, and malt bonbons are given.

CHEMICAL ABSTRACTS.

Detection of Formic Acid in Acetic Acid. M. POLINSKI (*Chem. Analyst*, 1920, **29**, 4).—Formic acid is easily oxidised by a mixture of sulphuric and chromic acids, which does not attack acetic acid. Twenty c.c. of the sample, containing not more than 6—8% of acetic acid (if it is concentrated, the sample must be diluted with water to prevent reduction of the chromic acid by propionic acid or other impurities), are mixed with 20 c.c. of concentrated sulphuric acid and 2—3 c.c. of 50% chromic acid solution. If formic acid is present, carbon dioxide is evolved and green chromic sulphate formed. CHEMICAL ABSTRACTS.

Naphthalenesulphonic Acids. III. Alternative Method for the Detection of Naphthalene-2 : 7- and -1 : 6-disulphonic Acids. JOSEPH A. AMBLER (*J. Ind. Eng. Chem.*, 1920, **12**, 1194—1195. Compare this vol., ii, 68).—A portion of the acetone-insoluble dry salts of the acids is boiled with 5 c.c. of a mixture of 4 volumes of 95% alcohol and 1 volume of water, the solution is filtered, and the filtrate cooled; the β-naphthylamine salt of the 2:7-disulphonic acid crystallises from the solution. Another portion of the dry salts is covered with water, boiled, and the mixture titrated with N/1-sodium hydroxide solution; the mixture is filtered, and the filtrate evaporated to dryness. The dry residue is dissolved in twice as much water as the volume of N/1-sodium hydroxide solution used, and the solution treated with an equal volume of concentrated sulphuric acid. The sodium salt of the naphthalene-1:6-disulphonic acid crystallises gradually from the cooled mixture, whilst the 2:7-acid remains in solution.

W. P. S.

General and Physical Chemistry.

Determination of the Refraction of Dissolved Substances, particularly Colloidal Substances. Robert Wintgen (*Kolloid Zeitsch.*, 1921, **28**, 5—6).—The author discusses the discrepancy found by Lifschitz and Beck (A., 1920, ii, 205) between their results for the refraction of certain colloidal solutions and those previously published by the author (A., 1915, ii, 751). It is shown that an error in n_L has the greatest effect on the accuracy of the results, and assuming maximum errors for the values of p, d_L, and n_L, the author has calculated the refractions of the colloidal solutions previously measured. The experiments have all been repeated, and a further set of results obtained which agree with previous measurements better than the values calculated on the basis of the maximum errors. J. F. S.

The Series Spectra of the Elements. A Lecture delivered before the German Physical Society, April 27th, 1920. N. Bohr (*Zeitsch. Physik*, 1920, **2**, 423—470).—The author reviews the present state of knowledge concerning the origin of spectral series. The application of the quantum hypothesis to the nuclear conception of the atom, combined with the assumption of a series of stationary conditions of the electronic orbits, has afforded a completely satisfactory explanation of the origin of the hydrogen spectrum. Radiation is emitted when the electron is displaced from one of the assumed stationary orbits to another, and the frequencies and the intensities of the spectral lines calculated are in strict accord with observation. The spectral series of lines of any elements of higher atomic number than hydrogen are all of frequencies ν, such that ν is given by the relation first advanced by Rydberg and Ritz, namely, $\nu = f_{K''}(n'') - f_{K'}(n')$, where n' and n'' are whole numbers, and $f_{K'}$ and $f_{K''}$ two functions the limits of which, when n' and n'' are large, are zero. The complete spectrum is derived from this expression by the combination principle of Ritz, every possible combination of $f_{K'}(n')$ and $f_{K''}(n'')$ being substituted in the expression. An explanation of the origin of the principal series, the sharp subordinate series, and the diffuse subordinate series of lines in the case of sodium is advanced by the consideration of a series of stationary conditions of the electronic orbits for which n and k are whole numbers. The assumptions of the theory are supported, not only by the emission spectra of the elements, but by the phenomena of selective absorption, the production of spectra by electronic bombardment of the atoms, and the phenomena of resonance spectra, as investigated by Wood and Strutt in the case of sodium vapour. The production of spectra and of ionisation by electronic impacts, first studied by Franck and Hertz, are in conformity with the assumptions of the

theory. The later work of Davis and Goucher, and similar experiments, afford direct evidence for the reality of the stationary conditions assumed in the theory developed. The author has recently investigated the effects of disturbing forces exerted on the electrons, as these are exhibited by the series of lines emitted by the element, in the case of hydrogen. Examining the effect in the case of the hydrogen atom, a result is obtained for the resultant series of spectral lines corresponding exactly with the result deduced by Epstein and Schwarzschild for the Stark effect in the hydrogen lines. The state of polarisation of the radiation in the Stark effect, as determined by Epstein, is likewise in accord with the deductions of the principle of correspondence. The application of this principle to the intensities of the various components has been studied by Kramers. The author proceeds to the consideration of the effect of a uniform magnetic field on the hydrogen lines, and likewise the effect of a small disturbing centrally symmetrical field of force on the hydrogen spectrum. It is pointed out that in this treatment, the specification of the stationary states does not correspond exactly with that of Sommerfeld, Epstein, and Debye. The effect of external forces on the fine structure of the hydrogen lines results, in general, in the stationary conditions being no longer sharply defined, the lines consequently losing their sharp definition. When the disturbing field is simple in character, this is not so. The mathematical development of the series spectra of the elements other than hydrogen is complicated, owing to the interaction of the various electrons. Reference is made to the work of Sommerfeld and Rubinowicz. Stark has studied a new series of combination spectrum lines, analogous to the combination tones of acoustics, produced by subjecting the radiating atoms to an intense electric field. The spectrum of helium comprises two series of lines, one a series of single lines and the other a series of doublets. The two series arise owing to mutual actions and reactions of the respective electrons in their orbits, whereby the respective orbits are perturbed. These disturbances have been investigated by the author and Kramers. The analytical difficulties become accentuated when atoms of still higher atomic numbers are being considered. J. S. G. T.

The Development of the Röntgen Spectral Series with Increasing Atomic Number. W. Kossel (*Zeitsch. Physik*, 1920, **2**, 470—480).—A critical discussion of the nature and origin of the characteristic *K*, *L*, *M*, and *N* *X*-radiation spectra of the elements. In general, the square roots of the respective characteristic frequencies are linearly related to the respective atomic numbers of the elements. These linear relationships, however, exhibit discontinuities corresponding to certain atomic numbers. The discontinuity in the case of the *K*-radiation corresponds with the atomic number 2 (He). In the cases of the *L*- and *M*-radiations, the respective discontinuities correspond with the atomic numbers 11 (Na) and 18 (Ar). The author concludes that in the case of neon, the mechanism of the second innermost

electron, and in the case of argon, the mechanism of the third innermost electron, is the source of the softest radiation.

J. S. G. T.

Influence of an External Field on the Rotation Spectrum. Analogy to the Stark Effect. GERHARD HETTNER (*Zeitsch. Physik*, 1920, **2**, 349—360).—On the assumption that a gaseous molecule possesses an electric moment, the author shows mathematically that, on Bohr's theory, an external electric field should produce a displacement and a multiplication of the spectrum lines due to the rotation of the molecules. The calculated effect should be readily detectable by means of Imes' apparatus in the short-wave ultra-red absorption lines in the cases of hydrogen chloride, bromide, and iodide.

J. S. G. T.

Influence of an Electrical Field on the Fine Structure of the Hydrogen Lines. H. A. KRAMERS (*Zeitsch. Physik*, 1920, **3**, 199—223).—Mainly a theoretical paper, in which the structure of the hydrogen lines is considered from the point of view of the relativistic Stark effect. The components of a given line in a weak electric field are split into one or more sharp, polarised components, which are displaced proportionally to the square of the force. New components thereby appear the intensity of which increases proportionally to the square or higher power of the electrical force. The components remain sharp and polarised with increasing field intensity, and eventually come more and more into the positions of the components demanded by the unrelativistic Stark effect. The distance of these components from the unresolved line increases proportionally with the first power of the field intensity.

J. F. S.

The Regularity in the Stark Effect on the Spectral Lines of Hydrogen and Helium. USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 187—199).—A theoretical paper in which results of experiments on the Stark effect on hydrogen and helium lines, recorded in previous papers (A., 1918, ii, 253; 1919, ii, 125, 379), are discussed. Equations are obtained connecting the displacement, in wave number, of a component with the strength of the electric field, the term number of the series, and the integral number of the component. In the case of the hydrogen lines of the Balmer series, the lines H_α, H_β, and H_δ fit the equations well, but in the case of H_γ there is some divergence with a few of the components. In the helium series, agreement between the observed displacements and those calculated from the equations is sometimes good, but there are many gaps in the observed components for some of the lines. It is noteworthy that the equations for both hydrogen and helium series contain the same constant, 0·673, which is nearly equal to that, 0·660, found by Epstein, theoretically, for the Balmer lines (*Physikal. Zeitsch.*, 1916, **17**, 148).

E. H. R.

Spectrum of Chlorine. I. Emission and Absorption Spectra. MASAMICHI KIMURA and MITSUHARU FUKUDA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 155—158).—Using a tube with electrodes of sodium chloride or another metallic chloride, a photographic comparison of the emission and absorption spectra of chlorine was made. The emission band becomes intense as the region where the absorption gets strong is approached; in the yellow to red region, where the gas is very transparent, the band emission is very faint, whereas in the opaque blue to violet region the band emission is very strong. There is thus a general correspondence between the two spectra, though they are not exactly complementary. E. H. R.

Spectrum of Chlorine. II. The Influence of Magnetic Fields on Spectral Lines of Chlorine. MASAMICHI KIMURA and MITSUHARU FUKUDA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 159—161).—The magnetic separation of single lines in the chlorine spectrum was examined, using tubes similar to those employed for examining the bromine spectrum (below) provided with salt electrodes. Photographs were taken with field strengths varying from 2000 to 6000 gauss. The lines examined were $\lambda\lambda$ 4781, 4786, 4794, 4896, 4904, 5078, 5218, 5221, and 5392. All the lines except λ 4786 gave magnetic triplets of wider specific separations than that of a normal triplet. The separation was proportional to the strength of the magnetic field in each case. E. H. R.

Spectroscopic Confirmation of the Isotopes of Chlorine. A. KRATZER (*Zeitsch. Physik*, 1920, **3**, 460—465).—The influence of the mass of the nucleus on the term of the line and band spectra has been theoretically investigated, and it is shown that the isotopes can be differentiated in the part due to the nucleus vibration and in favourable circumstances also in the rotation part. The measurements of the oscillation–rotation bands of hydrogen chloride due to Imes (*Astrophys. J.*, 1919, **50**, 251) are in complete accordance with the theory. J. F. S.

Doublets of the *K* Series of the Röntgen Spectra. NILS STENSSON (*Zeitsch. Physik*, 1920, **3**, 60—62).—The doublets of the *K* series of the Röntgen spectra have been measured for the elements from chlorine to copper with the exception of manganese. The values for the frequency difference of $K_{a_1a_2}$ are tabulated and compared with the $\Delta\nu$ values calculated by the Sommerfeld formula (*Ann. Physik*, 1916, [iv], **51**, 1), when it is found that the experimental values are always larger than the calculated values. This divergence is particularly marked in the case of the elements vanadium to nickel. The frequency differences of $K_{a_3a_4}$ are measured, but on account of the faintness of the photographs an accuracy of not greater than 0·1% is obtained. J. F. S.

The Spectrum of Bromine. I. Line and Band Spectra, Lines of Arc and Spark Types, and the Relations between the Lines. MASAMICHI KIMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 127—138).—For examining the spectrum of bromine an ordinary

Geisler tube was unsuitable, and a special type of tube was constructed in which metallic bromides were used as electrodes. Silver bromide was the best salt for this purpose, but sodium or potassium bromide was sometimes employed. The colour of the light varied with the vapour pressure and current density. With a very low pressure, the light from the capillary part of the tube was bluish-green and from the wider part chamois-yellow, but with increasing pressures the capillary light became deep pink, whilst a pink glow was diffused from the wider part. The spectra from these different kinds of glow were photographed and the lines tabulated. The intense lines of the blue spectrum lie under λ 4800, but in the pink spectrum they extend over the entire visible range. The strong lines characteristic of the pink spectrum are at $\lambda\lambda$ 6632, 6560, 6351, 6150, 4478, 4473, but a number of other intense lines in the blue region are common to both blue and pink glows. The spectra of the pink glow from the capillary and wide portions of the tube are not precisely similar, whilst the chamois-yellow glow from the wide tube shows a mixed line and banded spectrum. The banded portion extends from about λ 5000 to λ 6600, and has a fluted appearance similar to that of the iodine banded spectrum. A comparison of the banded spectrum with the absorption spectrum of bromine shows that these do not correspond, but further discussion of this point is reserved until more experiments have been made. The stronger lines in the pink spectrum are considered to be of the arc type, whilst the lines which are enhanced in passing from the pink to the blue glow are of the spark type. The lines of the arc type when plotted according to their frequencies fall into a number of well-marked groups of equal widths, and between pairs of lines in adjacent groups there is found a nearly constant frequency difference. E. H. R.

The Spectrum of Bromine. II. Line Structures and the Zeeman Effect. MASAMICHI KIMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 139—149).—The structures of a number of lines in the bromine spectrum were examined, using a 40-plate echelon grating. At least twelve lines between λ 6632 and λ 4674, all of the arc type, were found to have complex structures. The influence of the magnetic field on the complex lines $\lambda\lambda$ 6632, 6560, 6351, and 6150 was studied. Though all having a similar structure, the lines were not all similarly affected. In all cases satellites were very sensitive to the action of the field. In a strong magnetic field they always gave triplets. The Zeeman effect was also studied on a number of single lines, between $\lambda\lambda$ 5600 and 4600; they all showed magnetic triplets with wider separation than that of the normal triplet. E. H. R.

The Distribution of Charged Ions in the Path of an Electric Discharge through a Tube containing Bromine Vapour. MASAMICHI KIMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 151—153).—Adopting Stark's view that the emission centres of

spectral lines of spark type are doubly or triply charged atomic ions, and that lines of the arc type are emitted by singly charged atomic ions, the distribution of the different kinds of charged ion in the bromine spectra previously described (preceding abstracts) is discussed. E. H. R.

Arc and Spark Lines of Iodine. MASAMICHI KIMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 167—168).—The effect on the spectrum of iodine of constricting a portion of the discharge tube was studied, and it was found that in the light emitted from the constricted portion of the tube, the spark lines were enhanced, whilst those of the arc type were suppressed. The spark lines intensified were those corresponding with λλ 5178, 5185, 5199, 5216, 5678, 5690, 5710, 5739, 5950, 6075, whilst those of the arc type suppressed were λλ 4862, 4897, 4917, 5119, 5235, 5894, and others. Similar changes of the intensity of distribution in the spectrum were brought about by sending condensed discharges through an iodine tube having no constricted portion. As the discharge became heavy, the maximum intensity was displaced towards the short wave-length side of the spectrum. E. H. R.

Electrical States of Iodine Vapour when Emitting Line and Band Spectra. KOMATARO MAKINO (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 169—171).—The emission of line or band spectra by iodine vapour under the influence of an electric discharge depends on the width of the discharge tube and the current density. Using a glow oscilloscope and a falling-plate camera, the instantaneous current strengths in partial discharges emitting the line and band spectra of iodine were compared, and it was found that the current in a partial glow giving the line spectrum is about three times that of the band discharge. Potential gradients in the path of the discharges were also measured, and it was found that the energy required to emit spark lines is five or six times that required for the band spectrum. E. H. R.

Ultra-red Rotation Spectra of the Hydrogen Haloids. A. KRATZER (*Zeitsch. Physik*, 1920, **3**, 289—307).—A theoretical paper in which it is shown that it is probable that the missing line in the centre of the band of the rotation–oscillation bands is due to the quantum spring $1 \longrightarrow 0$ for emission and $0 \longrightarrow 1$ for absorption. The energy of a rotating and simultaneously vibrating molecule is expressed as a general force law between nuclei (unharmonic oscillators) by means of the quantum number of the rotation and vibration. This expression is used to construct a series formula for the ultra-red rotation–oscillation bands. This formula has been tėsted on the measurements of Imes (*Astrophys. J.*, 1919, **50**, 251) for hydrogen fluoride, chloride, and bromide, and an agreement between theory and experiment is obtained. It is suggested that the quantum spring $1 \longrightarrow 2$ is observed in the oscillations of Imes. The moment of inertia and the distance between the nuclei has been calculated for the hydrogen haloids. J. F. S.

The Einstein Gravitational Displacement in the Case of the Nitrogen Band λ = 3883 Å.U. in the Sun's Spectrum. L. GREBE and A. BACHEM (*Zeitsch. Physik*, 1920, **2**, 415—422).—The absence of pressure and pole effects in the case of the nitrogen band λ=3883 Å.U. makes this band suitable for the investigation of a possible Einstein gravitational effect on the sun's spectrum. A comparison by a Rowland grating of the sun's spectrum with the cyanogen band spectrum yielded results for the displacement in the red end of the spectrum agreeing with those of Schwarzschild, but somewhat greater than those of St. John. These results, in agreement with those of Schwarzschild, St. John, Evershed and Royds, indicate that different lines in the spectrum are differently displaced, a result which is not to be attributed to the existence of a different Doppler effect in the case of the various lines, as these all originate in the same source. The authors, by a microphotometric comparison of the cyanogen band emission spectrum with the sun's absorption spectrum, conclude that nine only of the thirty-six cyanogen lines previously measured are sufficiently free from objection to be used in the present connexion. Employing these nine lines only, the authors obtain the mean value 0·56 km. per sec. as the displacement, compared with the values 0·63 km. per sec. deduced from Schwarzschild's observations, 0·67 km. per sec. deduced from the observations of Evershed and Royds, and the value of 0·32 km. per sec. given by St. John's results, in each case employing only such of the observed lines as are included in the nine free from objection. The authors conclude that the displacement predicted by Einstein is correct, both in magnitude and direction. J. S. G. T.

Conditions for the Excitation of the Mercury Lines. R. SEELIGER (*Zeitsch. Physik*, 1920, **2**, 405—414).—The mercury spectrum comprises a series of triplets, constituted of a principal and two subordinate series, and a series of single lines made up of a principal and two subordinate series. In addition, there are the spark lines 4339 and 4078, and extraneous lines 2847 and 2536. The respective intensities of these lines in the dark column and the luminous glow of the electric discharge between iron electrodes in mercury vapour contained in a discharge tube of uviol glass have been investigated. The results are given in the form of curves showing how the intensities of the lines vary with distance from the cathode at which the intensity is measured. The maximum intensity in the case of the lines of the first triplet subordinate series occurs nearer the cathode than is the case with the second triplet subordinate series. A similar result holds in the case of the first and second subordinate series of single lines. The maxima occur at increasing distances from the cathode in the following order: 1st subordinate series of single lines, 1st subordinate series triplets, 2nd subordinate series of single lines, 2nd subordinate series of triplets, 2536, 2847. This order is the inverse of the order of the critical emission potentials. The lines 4078 and 2536 do not

belong to a combination series. In pure mercury vapour the respective maxima are very sharply defined, and all occur at approximately the same place. J. S. G. T.

Regularities in the Infra-red Spectra of Gases and their Significance. GERHARD HETTNER (*Zeitsch. Physik*, 1920, **1**, 345—354).—A theoretical paper, in which the vibration of one atom of any polyatomic molecule is investigated on the assumption that any force is active between the atoms and without the assumption of infinitely small amplitudes. On the basis of the classical theory and also from Planck's second quantum hypothesis, whole number relationships are found for the frequencies of the infra-red absorption bands brought about by these vibrations. The relationships are shown to hold in all cases where they are applicable. In particular, all the red and infra-red bands in the water-vapour spectrum can be explained. J. F. S.

Characteristic Ultra-red Frequencies of Ammonium Salts. O. REINKOBER (*Zeitsch. Physik*, 1920, **3**, 1—8).—The reflexion spectra of the short wave-length portion of the ultra-red has been determined for ammonium chloride, bromide, iodide, fluoride, sulphate, and nitrate. In all cases but that of the fluoride, the measurements were made over the range 1 μ—16·5 μ; in the case of the fluoride, on account of its hygroscopic character, only one measurement was made, namely, at 7·0 μ. The substances were compressed to circular plates 37 mm. diam., and illuminated by a Nernst burner. The measurements were made with a Feuss mirror spectrometer fitted with a rock-salt prism and a vacuum thermopile. It is shown that vibrations characteristic of the ammonium radicle occur at 3·2 μ, 5·8 μ, and 7·0 μ. Ammonium nitrate showed, in addition to the hitherto known frequencies of the nitrate radicle, a very weak frequency at 9·7 μ. An accuracy of 0·01 μ is claimed for the measurements. J. F. S.

Absorption Boundaries in the *L*-series. G. HERTZ (*Zeitsch. Physik*, 1920, **3**, 19—25).—The absorption boundaries in the *L*-series have been determined for the elements cæsium, barium, lanthanum, cerium, praseodymium, and neodymium. The three absorption boundaries are nearly equidistant. When the $\sqrt{v/N}$ values are plotted against the atomic numbers, it is found that the new values fall on the same curves as those previously obtained for the heavier elements. The curves for the boundaries A_2 and A_3 are parallel to one another throughout the whole length from U (92) to Cs (55), whilst the A_1 and A_2 curves converge with decreasing atomic number. J. F. S.

Absorption Boundaries of the *L*-series. ADOLF SMEKAL (*Zeitsch. Physik*, 1920, **3**, 243—246).—A theoretical paper in which it is shown that the measurements of the absorption boundaries of the *L*-series spectrum (Hertz, preceding abstract)

confirm the assertion made by the author (*Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 2*a*) that only three L boundaries exist, and that the Δ doublet is not real. The oft-quoted intersection of the L curves in the $\sqrt{\nu/R}-z$ diagrams are explained by the course of the L absorption boundaries. J. F. S.

Precision Measurements in the *L*-series of the Röntgen Spectra: Elements Tungsten to Copper. ELIS HJALMAR (*Zeitsch. Physik*, 1920, **3**, 262—286).—Measurements of the L-series Röntgen spectra have been made for the elements tungsten to copper, with the exception of gallium, thulium-*I*, thulium-*II*, krypton, and xenon. The results are recorded in a number of tables, and then considered theoretically. J. F. S.

Absorption of *X*-rays by Chemical Elements of High Atomic Numbers. WILLIAM DUANE, HUGO FRICKE, and WILHELM STENSTRÖM (*Proc. Nat. Acad. Sci.*, 1920, **6**, 607—612). —The critical absorption wave-length of X-rays, which is associated with the K-series of emission lines, has been determined for the elements uranium to tungsten. In the experiments, an ionisation spectrometer was used, and an X-ray bulb fed by a current of 140,000 volts. The following values for the K critical absorption wave-length have been found: tungsten, 1781×10^{-8} cm.; platinum, 1581×10^{-8} cm.; gold, 1532×10^{-8} cm.; mercury, 1491×10^{-8} cm.; thallium, 1448×10^{-8} cm.; lead, 1410×10^{-8} cm.; bismuth, 1372×10^{-8} cm.; thorium, 1131×10^{-8} cm.; and uranium, 1075×10^{-8} cm. The above values are the mean of values obtained in the first-, second-, and third-order spectra. J. F. S.

Use of Photo-electric Cells in the Measurement of Light Absorption by Solutions. HANS VON HALBAN and HERIBRANT GEIGEL (*Zeitsch. physikal. Chem.*, 1920, **96**, 214—232). —A method is described whereby the absorption of light by solutions may be determined rapidly and with great accuracy by the use of an alkali metal cell (sodium or potassium). It is shown that, using a constant source of light (nitralamp) and a sodium or potassium photoelectric cell, measurements may be made over the spectrum range 300—570 $\mu\mu$ for sodium and 360—630 $\mu\mu$ for potassium, but these ranges must be somewhat reduced if thick layers of solutions or homogeneous light is employed. It is also shown that this method may be used with advantage for measurements in the ultra-violet down to 253 $\mu\mu$ if a mercury vapour lamp is employed as the source of illumination. It is further shown by means of measurements with solutions of the yellow tetrabenzoylethylene and anthracene that the method may be employed by determining the extinction coefficient of solutions. J. F. S.

Photo-electric Conductivity and Phosphorescence. B. GUDDEN and R. POHL (*Zeitsch. Physik*, 1920, **3**, 98—103).— Using a calcium–sodium–bismuth phosphorescent substance, the

authors have shown that the maximum of phosphorescent excitement found by Lenard is also the maximum of photoelectric conductivity. This result has been obtained by working with very high electric fields, up to 16,000 volt/cm. If the return of electrons to a phosphorescent substance which has been continuously excited is accelerated by light, it is shown that the return of the electrons is reflected in an increased electrical conductivity of the phosphorescent substance. J. F. S.

Density and Specific Rotation of Mixtures of Liquids with One Optically Active Constituent. W. DEUTSCHMANN (*Zeitsch. physikal. Chem.*, 1920, **96**, 428—436).—A theoretical paper, in which it is shown that the specific rotation of mixtures of inactive and active substances may be calculated from the individual rotation values and the composition of the constituents of the mixture, if by composition is understood, not the analytical composition, but the composition as determined by the volume change. Thus from formulæ of the type $\Phi = z_{a_1}\phi_{a_1} + z_{a_2}\phi_{a_2} + z$ the molecular rotation may be calculated, where Φ is the molecular rotation of the mixture, z, z_{a_1} and z_{a_2} the percentage of associated molecules A_mB_n formed as in the equation $mA + nB = A_mB_n$, the percentage of simple molecules A after mixing and the percentage of double molecules after mixing, and ψ, ψ_{a_1} and ψ_{a_2} the molecular rotations of the respective constituents, the molecular species B, whether simple or multiple, being inactive. The formula is tested for mixtures of benzene and turpentine, and good agreement with fact is obtained. J. F. S.

Influence of Temperature on Photochemical Processes. XII. J. PLOTNIKOW (*Zeitsch. wiss. Photochem.*, 1920, **20**, 125—139). —A theoretical paper in which the temperature-coefficient of photochemical processes is discussed. It is shown that the non-illuminated reactions have temperature-coefficients which increase with decreasing temperature and approach unity at very high temperatures. Photochemical reactions may be arranged in three groups with temperature-coefficients, $1·03 \pm 0·03$, $1·20 \pm 0·03$, and $1·40 \pm 0·03$ respectively. The first group ($TC = 1·03 \pm 0·03$) includes among other reactions, anthracene polymerisation, decomposition of sodium hypochlorite, and the reactions of the photographic plate, the second group ($TC = 1·20 \pm 0·03$) the decomposition of ozone in the presence of chlorine, and the third group is made up chiefly of reactions in which one of the halogens plays an important part. The author considers that the temperature-coefficient is a characteristic constant of photochemical reactions. The three groups may in all probability be reduced to two, since the second, $1·20 \pm 0·03$, is the same as the temperature-coefficient of diffusion, and the reactions to which this coefficient applies are for the most part gaseous. The influence of the wave-length of the light on the coefficient is considered, and it is shown that in the case of photographic plates the temperature-coefficient with white light is 1·06, with plates

sensitised with pinachrome for blue light $\lambda = 436\ \mu\mu$, $TC = 1\cdot04$, for yellow light $\lambda = 579\ \mu\mu$, $TC = 1\cdot08$, and for green light $\lambda = 546\ \mu\mu$, $TC = 1\cdot08$. For plates which have been exposed to very subdued light, the temperature-coefficient for blue light is 1·03, yellow light 1·04, and green light 1·04. J. F. S.

The Action of Light on Sparingly Soluble Oxides in Solutions of Silver Salts. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **114**, 151—152).—When ignited zinc oxide is left in a solution of silver nitrate or silver sulphate in subdued light, it remains white for a whole day, but in bright light it quickly becomes grey, and, after a quarter of an hour, black. Lead oxide (litharge) blackens in the same manner, even in subdued light, but less rapidly than in sunlight, and ferric oxide, bismuth oxide, Bi_2O_3, antimonic oxide, and yellow mercuric oxide change in colour more slowly. The blackening is due to the deposition of silver oxide. An ionic exchange appears to take place at the surface of the oxide, controlled, probably, by the electric potentials of the reacting substances. The velocity of the reaction depends on the tendency of the silver oxide to crystallise in the lattice form appropriate to the medium in which the deposition takes place. E. H. R.

Reduction of Sodium Silver Thiosulphate by Hyposulphite. II. ALBERT STEIGMANN (*Kolloid Zeitsch.*, 1921, **28**, 29—31. Compare this vol., ii, 13).—A discussion of the physical development of the latent photographic image by sodium hyposulphite in plates and papers after they have been fixed. The silver required for the development is obtained from the silver sodium thiosulphate of the fixing bath. J. F. S.

Photo-chemistry of Tetra-benzoylethylene. I. HANS VON HALBAN and HERIBRANT GEIGEL (*Zeitsch. physikal. Chem.*, 1920, **96**, 233—250).—The colour changes which tetrabenzoylethylene undergoes under the influence of light have been investigated. It is shown that the conversion of colourless tetrabenzoylethylene into a yellow compound by the action of light is not reversible. If the yellow compound is kept in the dark, it again becomes colourless, but will not then take on the yellow colour if it is again subjected to light. In light, a rapid decolorisation is superimposed on the decolorisation in the dark, by which the same product is in all probability formed. The processes may be represented by the scheme:

$$\underset{\text{Colourless.}}{A} \xrightarrow{\text{light}} \underset{\text{Yellow.}}{B} \xrightarrow[\text{light}]{\text{dark and}} \underset{\text{Colourless.}}{C}$$

The substance B was isolated, and found to have the same molecular weight as A. The absorption spectra of A, B, and C have been photographed, and that of B determined by means of the photoelectric cell previously described (this vol., ii, 145). The

absorption spectra were examined in alcoholic solution; A and C exhibit no marked absorption in the visible region, whilst B has an absorption maximum in the blue. The molecular extinction coefficient of B is found to be $1{\cdot}813 \times 10^4$. The course of the decolorisation, both in light and in the dark, was followed by means of a photoelectric cell, and it is shown that the dark reaction is of the first order. Its velocity depends markedly on the solvent, and is increased by the presence of acids. Oxygen retards the light reaction, but is without influence on the dark reaction. The velocity of formation of B in light is uninfluenced by the presence of oxygen. The reaction $B \longrightarrow C$ under the conditions of the present experiments is also unimolecular, and it has a very much greater velocity when subjected to even a weak illumination than the dark reaction. J. F. S.

Direct Determination of the Range of α-Rays in Solids. H. Rausch von Traubenberg (*Zeitsch. Physik*, 1920, **2**, 268—276).—A small-angled wedge of the solid was arranged with its lower face parallel to, and at a few millimetres distant from, a plane surface activated by means of radium-*C*. The upper face of the wedge was in contact with a zinc sulphide phosphorescent screen. The range of the α-rays in the solid was determined by observing the distance of the line of demarcation between the light and dark regions of the screen from the angle of the wedge. Correction was made for the thickness of air between the lower face of the wedge and the source of α-radiation. The effect of β-radiation was eliminated by placing the apparatus between the poles of a powerful magnet. The following results were obtained for the respective ranges expressed in 10^{-4} cm. in the various elements stated: lithium, 129·1; magnesium, 57·8; aluminium, 40·6; calcium, 78·8; iron, 18·7; nickel, 18·4; copper, 18·3; zinc, 22·8; silver, 19·2; cadmium, 24·2; tin, 29·4; platinum, 12·8; gold, 14·0; thallium, 23·3; lead, 24·1. The experimental results can be correlated with the atomic numbers of the respective elements by the formula

$$R_s = \sqrt[2]{A_s/d_s} \cdot \sqrt[2]{Z_s/A_s} \cdot \sqrt[2]{A_N/Z_N} \cdot d_N / \sqrt[2]{A_N} \cdot R_N,$$

where R_s, A_s, d_s, and Z_s are respectively the range, atomic weight, density, and atomic number of the substance, the subscript N referring to the corresponding physical constants in the case of hydrogen, for which Taylor's value of $R_N = 30{\cdot}9$ cm. at 15° and 760 mm. is employed. The results in the cases of helium and lithium do not satisfy this relation. It is surmised that these anomalies may originate in the production of secondary α-radiation, due to impact of the primary α-radiation. J. S. G. T.

Application of the Displacement Rule to the Case of Substances Emitting Simultaneously both α- and β-Rays. Otto Hahn and Lise Meitner (*Zeitsch. Physik*, 1920, **2**, 60—70). —Radium emits both α- and β-radiations. The application of the displacement rule for the atomic weight of the resulting transforma-

tion products, indicates that these should comprise 92% of radium emanation due to the emission of α-radiation, and 8% of a tervalent isotope of actinium arising from the emission of β-radiation. In the case of radio-actinium, the emission of β-radiation should result in the conversion of 13% of the transformed radio-actinium into a quinquevalent isotope of proto-actinium. A search for such transformation products arising from the emission of β-radiation in the case of radium and radio-actinium led in each case to a negative result—no trace of such anticipated transformation products being obtained in either case. The authors are unable to advance any satisfactory explanation of these negative results, but suggest the possibility of the quick-moving β-rays originating in a secondary manner by the transportation of energy to the electrons by the α-rays, and not having a H nucleus attached to them. J. S. G. T.

Relationship of the Actinium Series Branch of the Uranium–Radium Series. ADOLF SMEKAL (*Physikal. Zeitsch.*, 1921, **22**, 48—51).—A theoretical paper in which the disintegration of Ur-II is considered. The author makes the assumption that in the disintegration of Ur-II to form Ur-Y, an X_3 particle is emitted, whilst an α-particle is emitted in the disintegration to ionium. This involves the further hypothesis that the nucleus of Ur-II is made up of fifty-seven α-particles and two X_3-particles. On the basis of these hypotheses the author deduces the fraction of the Ur-II disintegration which goes to form the actinium series, and finds a value 3·4%, which falls between the most recent values 3·0—4·2%. Radio-actinium furnishes a quantitative proof of the possibility of the existence of radioactive X_3-rays. J. F. S.

The Enumeration and Range of the Recoil Atoms of Thorium-*C* and Thorium-*C′*. WERNER KOLHÖRSTER (*Zeitsch. Physik*, 1920, **2**, 257—263).—A slightly modified form of the apparatus embodying the point discharge, employed by Geiger (A., 1913, ii, 745) and Kovarik and McMeehan (A., 1915, ii, 605) for counting α- and β-particles, was employed to determine the number and range of recoil atoms of thorium-C and thorium-C'. Aluminium foil, activated for twelve hours at low tension by a mesothorium preparation, served as source of the radiation. The recoil atoms were counted in hydrogen for pressures between 4 mm. and 74 mm. of mercury. The resultant curve in which the numbers of recoil atoms are plotted as ordinates against the appropriate pressures as abscissæ is made up of a number of horizontal portions corresponding with the respective numbers of recoil atoms, 0, 60, and 100, joined by very steep portions corresponding with respective pressures of 61 mm. and 35 mm. of mercury. Two kinds of recoil atoms appear at these pressures. These correspond with the α-radiation of thorium-C' and thorium-C respectively, in agreement with the relative proportions of thorium-C' and thorium-C present in the active preparation. It is concluded that a recoil atom results from each atom of thorium-C and thorium-C' transformed by the emis-

sion of an α-ray. The respective ranges of recoil were determined by employing various distances between the active preparation and the discharge point of the counting device, the pressure in the apparatus being suitably adjusted so that the recoil was registered. In this manner the average range of recoil in hydrogen at 15° and 760 mm. was found to be $0{\cdot}55_3$ mm. in the case of thorium-*C* and $0{\cdot}96_3$ mm. in the case of thorium-*C′*. The corresponding ranges in air at 15° and 760 mm. are $0{\cdot}12_9$ mm. and $0{\cdot}22_4$ mm. J. S. G. T.

Radioactive Facts and Nuclear Structure. GERHARD KIRSCH (*Physikal. Zeitsch.*, 1921, **22**, 20—23).—In a previous paper (A., 1920, ii, 577) the author showed that the atomic nucleus consisted chiefly of some fifty α-particles and some twenty binding electrons, to which in the radium and actinium series several H particles have to be added. The present paper is a continuation of the discussion applied to the several radioactive series. J. F. S.

Potential of Excitation of Helium. J. FRANCK and P. KNIPPING (*Zeitsch. Physik*, 1920, **1**, 320—332. Compare A., 1920, ii, 20; Horton and Davies, A., 1919, ii, 210).—The resonance and ionisation potentials of pure helium have been determined, and it is shown that two resonance potentials exist at the values 0·8 volt removed from one another, a result which is demanded by the two series spectra of helium. The potential curve shows calculated breaks at 20·45, 21·25, 21·85, 23·7, and 25·3 volts, whilst the experimental curve has breaks at 20·45, 21·25, 21·9, 23·6, and 25·3 volts. The point 20·45 does not show until a little gaseous impurity is allowed to mix with the helium, but it is held that the break is due to the helium, and not to the impurity. J. F. S.

The Properties of Protoactinium. II. Life Period and Content in Uranium Minerals. OTTO HAHN and LISE MEITNER (*Ber.*, 1921, **54**, [*B*], 69—77. Compare A., 1919, ii, 209; 1920, ii, 147).—It has been shown previously that only 3% of the atoms of uranium disintegrating pass through the protoactinium, actinium series, but the period of average life of protoactinium could only be fixed within the limits of 1200 and 180,000 years. By separation of the protoactinium from uranium salts of approximately known age (three preparations, one of the nitrate at least twenty years old, the second of the nitrate at least fifty-two years old, and the third consisting of a mixture of yellow uranium oxide and uranium acetate, each about sixty years old), and measurement of its activity in comparison with that of uranium, it has been found possible to estimate the half-life period of protoactinium, the mean of three concordant experments being about 12,000 years. This value is to be regarded as the lower limit. From this datum and the known disintegration ratio of the actinium series to the uranium series it is possible to calculate the protoactinium content of uranium minerals. It is thus found that one ton of uranium in any uranium mineral contains 72 mg. of protoactinium; the corresponding figure for radium is 330 mgm. H. W.

Spray-electricity of Solutions of Electrolytes. H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 658—662).—A continuation of previous work in which it was attempted to correlate the odour of different organic substances with the positive electric charge developed when an aqueous solution of the substance is sprayed (compare A., 1918, ii, 351). Inorganic acids and bases appear not to develop any charge when sprayed, at any concentration, with the possible exception of hydrochloric acid. Among organic acids are found some, including benzoic, salicylic, lactic, and the fatty acids, which in concentrated solutions give a positive charge and in weaker solutions a negative charge, with a zero transition point at a definite concentration. These phenomena can be explained on the hypothesis that the positive charge of the spray is due to whole molecules, whilst the negative charge is due to the dissociated anions which lie nearest the surface of the droplets composing the spray. Concentrated solutions of some inorganic salts when sprayed have a slight, though distinct, negative charge, whilst others do not give any charge. E. H. R.

Thermal and Electrical Conductivity of Lithium between 20° and 373° Absolute. WALTHER MEISSNER (*Zeitsch. Physik*, 1920, **2**, 373—379).—Determinations were made of the thermal and electrical conductivities of two rods of lithium, about 5 cm. long and 0·5 mm. diameter, the one being employed between 56° and $-193°$ and the other between 100° and $-250°$. A modified form of the apparatus previously employed by the author was employed, precautions being taken to maintain the surface of the metal untarnished during the course of the determinations, and to secure good electrical connexions between the metal and the leads. Samples of lithium supplied by Kahlbaum were employed. It is recognised that they contained perceptible impurities. The temperature-coefficient between 0° and 100° was found to be practically constant and equal to $4·35 \times 10^{-3}$. The corresponding values of the temperature-coefficients between 273° and 90·9°, 80·14°, 20·42° absolute were found to be respectively $4·21 \times 10^{-3}$, $3·85 \times 10^{-3}$, and $0·25 \times 10^{-3}$. The value of the quotient of the thermal conductivity by the product of electrical conductivity and the absolute temperature increased from $2·29 \times 10^{-8}$ at 19·75° to $2·64 \times 10^{-8}$ at 101·26°. The corresponding values at 90·90° and 20·42° absolute were $1·34 \times 10^{-8}$ and $0·63 \times 10^{-8}$. The absolute value of the specific electrical conductivity at 0° could not be determined owing to the irregular form of the specimens employed, but calculated values agreed within 10% with the value $11·7 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ given by Guntz and Broniewski (A., 1909, ii, 113). Using this value, the observations lead to the value 0·17 (grm. cm. deg. sec.)$^{-1}$ for the thermal conductivity of lithium at 0°. A comparison of the value of the temperature-coefficient of resistance obtained in the research with those of Guntz and Broniewski leads the author to conclude

that the specimens of lithium employed were of greater purity than that employed by the latter observers. J. S. G. T.

Electrical Conductivity of Solid Mixtures of Salts. A. Benrath and H. Tesche (*Zeitsch. physikal. Chem.*, 1920, **96**, 474—482).—The electrical conductivity of mixtures of lithium chloride and potassium chloride, sodium nitrate and lithium nitrate, lead chloride and stannous chloride, have been measured over a considerable range of temperature and over the whole range of compositions. The results indicate that conductivity isotherms similar to those for alloys do not suffice to represent the results in the case of mixtures of salts. The point at which the eutectic is formed is a well-characterised point in the conductivity isotherms, and if the curves are suitably drawn, they furnish information as to the part played by the individual components in the conductivity. J. F. S.

Recovery of Transmissivity in Passive Iron Wires as a Model of Recovery Processes in Irritable Living Systems. II. Ralph S. Lillie (*J. gen. Physiol.*, 1920, **3**, 129—143. Compare this vol., ii, 80).—Passive iron wires, when activated after prolonged immersion in nitric acid of 55—90 vols. % of acid, D 1·42, revert spontaneously to the passive state after a temporary reaction, which is transmitted rapidly over the whole length of wire. The duration of this reaction at any region decreases rapidly with increase in the concentration above a certain critical limit of 52—54%. In weaker acid, 50% and lower, the reaction continues uninterruptedly until all the metal is dissolved. Immediately after this automatic repassivation, the wire fails to transmit activation through more than a short distance (1—2 cm.); if left undisturbed in the acid, it recovers by degrees its power of transmission, as measured by the distance travelled by an activation wave, at first slowly, then more rapidly; eventually, after an interval varying with the concentration of acid and the temperature, the activation wave is transmitted through an indefinite distance, as before. The return of complete transmissivity in 55% acid occupies less than a minute at 20°; in stronger acid it is more gradual, requiring in 90% acid twenty minutes or more. This "complete recovery time" is nearly proportional to the excess of concentration of acid above the limiting value of 53—54%. In a given solution of acid, the rate of recovery exhibits a temperature-coefficient closely similar to that of most chemical reactions at this temperature, 3 at 20°, and also to that of the rate of recovery (refractory period) of irritable living tissues after stimulation (Q_{10}=about 3). Two definite phases are distinguishable in the recovery process: (i) the re-deposition of the continuous passivating layer of oxide or oxygen compound, and (ii) the progressive change of the newly passivated wire from the state of incomplete to that of complete transmissivity. The former phase is of brief duration, and is indicated by a sudden change in the

electrical potential of the wire from that of active to that of passive iron; this phase is succeeded by the second and more prolonged period, during which the passivating layer undergoes the progressive alteration associated with the recovery of transmissivity. This alteration appears to consist in a progressive thinning of the passivating film until a minimum thickness of probably one molecule is attained. Further thinning is prevented by local electrochemical oxidation. The phenomena of partial or limited transmission during the second phase of the recovery process show a close correspondence with the phenomena of conduction with decrement in irritable living tissues, such as nerve. Other analogies with the behaviour of irritable tissues, such as threshold phenomena, distinction between "local" and "propagated" effects, summation, and effects resembling electrotonus, are described. J. F. S.

Passivity. Researches on Iron and Nickel. C. A. Lobry de Bruyn (*Rec. trav. chim.*, 1921, **40**, 30—64).—The first part is a theoretical discussion of passivity based on the theory of Smits and his co-workers (compare A., 1914, ii, 165, 420, 611; 1915, ii, 39, 217; 1916, ii, 77; 1917, ii, 262; 1918, ii, 54).

The author finds for the equilibrium potential of iron in ferrous sulphate solution, when compared against a calomel normal electrode, the value $E_h = -0{\cdot}434$ volt (compare Richards and Behr, A., 1907, ii, 222). He has examined the influence of hydrogen and oxygen, variation in temperature, and presence of ferric ions on the equilibrium potential of iron (*loc. cit.*), and applies these results to a consideration of the passification of iron.

The fact that iron becomes passive in concentrated nitric acid may be attributed to two factors, namely, (i) that in nitric acid the concentration of the electrons is very feeble, and (ii) that activating influences do not make themselves felt.

The cathodic and anodic polarisation of iron is considered, and in the latter case a graph is given showing the variation in the potential of iron in solutions of ferrous sulphate and ferrous chloride, as measured against a calomel electrode at different current densities. In ferrous sulphate solution, when the current density reaches about 0·4 ampere per sq. cm., the electrode suddenly becomes passive, and if the current density is further increased, there is only a feeble further increase in the potential. In ferrous chloride solution, this sudden change is not observed, and even at the highest current densities used the electrode remains active.

In the passage into solution from an iron anode, the current yield is practically 100% when the iron is in the active state. When, however, it is in the passive state, the yield is only of the order of 1%, and varies with the sample of iron used. The potential of passive iron during anodic polarisation falls as the temperature rises, and curves are given showing the activation of iron under different conditions after anodic polarisation. W. G.

The Detection of Parts of Different "Nobility" in a Piece of Metal. S. Kyropoulos (*Zeitsch. anorg. Chem.*, 1920, **114**, 157—160).—Different parts of a piece of metal may exhibit different behaviour in certain solutions, on account of differences of electric potential. Thus, when a clean nail is placed in an agar gel containing potassium ferricyanide and phenolphthalein, the metal at the point appears more "noble" than that at the head; in the neighbourhood of the point a red colour develops, on account of the formation of free OH' ions, whilst along the surface of the nail a blue colour appears, due to the production of Fe'' ions. The difference is due to the greater degree of working to which the metal towards the head of the nail has been subjected. If potassium ferrocyanide is substituted for ferricyanide in the solution, it may be used to detect similar local differences in pieces of manganese, zinc, cadmium, aluminium, nickel, or copper. If a clean silver plate is scratched and immersed in an agar solution containing potassium iodide and phenolphthalein, the scratches show up as black lines on a bright ground, through the deposition, on the less "noble" worked parts, of silver iodide. With proper choice of indicators, the method should be generally applicable to the detection of chemical and physical inhomogeneity in the surface of a metal. E. H. R.

The Separation of Gases and the Production of Pressure Differences in the Positive Column in the Electrical Discharge in Rare Gases, and its Explanation on the Basis of Elastic Impacts of Electrons. Application to the Case of Isotopes of the Rare Gases. Franz Skaupy (*Zeitsch. Physik*, 1920, **2**, 213—217).—In a previous paper (A., 1916, ii, 469), the author has pointed out that two gases may be quickly separated when submitted to the effect of the discharge in a long discharge tube supplied with direct current, one gas collecting at the cathode, the other at the anode. The effect was attributed to the different ionisation potentials of the gases and the different tendencies exhibited by the respective neutral atoms to form negative molar ions. Assuming that the electrons moving towards the anode exert an appreciable pressure on the gas, it is shown that, due to impact of the electrons on the atoms of a gaseous mixture, the lighter atoms are more strongly urged thereby towards the anode. In the case of the rare gases, low atomic weight is characterised by high ionisation potential, and the resultant separation arises from the operation of both causes, impact and ionisation effects being both operative. From the point of view of separation originating in the electronic impacts on the atoms, separation of the isotopes of the rare gases should be easily possible. A simple relation is deduced between the pressure gradient in the positive column and the field strength. This takes the form $dp/dx = nXe$, where n is the number of electrons per unit volume, X the field strength, and e the ionic charge. J. S. G. T.

Thermodynamics of Normal Elements. VII. Temperature Formula of the Weston Normal Element and the Solubility Curve of $CdSO_4,\frac{8}{3}H_2O$. ERNST COHEN and J. J. WOLTERS (*Zeitsch. physikal. Chem.*, 1920, **96**, 253—258).—The authors criticise the temperature formula for the Weston normal element which was adopted by the International Conference on Electrical Units and Standards, 1908. This formula has the form $E_t = E_{20} - 0{\cdot}0000406(t-20) - 0{\cdot}00000095(t-20)^2 + 0{\cdot}00000001(t-20)^3$, and gives a maximum *E.M.F.* at $+3°$, which is in keeping with a minimum solubility of $CdSO_4,\frac{8}{3}H_2O$ at $+1°$. This solubility minimum is taken from results of Mylius and Funk (A., 1897, ii, 316). The authors criticise the accuracy of these determinations, and have redetermined the solubility of $CdSO_4,\frac{8}{3}H_2O$ at low temperatures and obtained the following values: $-3{\cdot}00°$, 43·047 grams per 100 grams solution; $-6{\cdot}00°$, 43·020 grams; $-9{\cdot}00°$, 43·008 grams; and $-12{\cdot}00°$, 43·029 grams. This gives a solubility minimum at $-9°$, and this value is in keeping with the temperature formula of Jaeger and Wachsmuth (*Ann. Phys.*, 1902, **9**, 1046), $E_t = E_{20} - 0{\cdot}000038(t-20) - 0{\cdot}00000065(t-20)^2$, which is therefore to be preferred before the formula at present adopted for the change of *E.M.F.* of the Weston normal cell with temperature.

J. F. S.

Thermodynamics of Normal Elements. VIII. ERNST COHEN, W. D. HELDERMAN, and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **96**, 259—274. Compare preceding abstract). The various factors necessary for a recalculation of the *E.M.F.* of the Weston cell at 18° have been redetermined with very refined apparatus. Among the data thus obtained are: heat of solution of potassium chloride in 200 molecules of water, -4397 cal. (mean of seven experiments); *E.M.F.* of the cell Cd-amalgam (8% Cd) | $CdSO_4$ solution (2·559%) | Hg_2SO_4Hg; 25°, 1·07175 volt; 20°, 1·07208 volt; 15·0°, 1·07239 volt; and in a second series of measurements: 25°, 1·07170 volt; 20·0°, 1·07202 volt; 15°, 1·07235 volt. These values give the relationship between *E.M.F.* and temperature as $E_t = 1{\cdot}07173 - 0{\cdot}0000645(t-25)$, from which the chemical energy of the combination at 18° is calculated as 50,298 cal. The combination Cd(γ) | $CdSO_4$ solution (2·559%) | Hg_2SO_4Hg has been measured, and the values 25°, 1·12273 volt; 15°, 1·12560 volt; and 20°, 1·12398 volt obtained. The heat change when 1 mol. of $CdSO_4$ dissolves in an unlimited quantity of $CdSO_4$, $440{\cdot}6H_2O$ is calculated to $Q_d = 10{,}627$ cal. The heat of solution of $CdSO_4$ in solutions of $CdSO_4$ of various concentrations at 18° is determined, and the difference between the heats of formation of $CdSO_4$ and Hg_2SO_4 is found to be 45,346 cal. The heat of hydration of anhydrous $CdSO_4$ to form $CdSO_4,\frac{8}{3}H_2O$ is found to be 7890 cal. Using the above data, the chemical energy of the Weston element is found to be 47,427 cal., using the international temperature formula, and

47,447 cal., using Jaeger and Wachsmuth's formula, whilst by the thermochemical method the value of 47,561 cal. is obtained.

J. F. S.

Thermodynamics of Normal Elements. IX. Temperature Formulæ of Normal Elements and the Specific Heat of the Salts contained in these Elements. ERNST COHEN, C. I. KRUISHEER, and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **96**, 437—470. Compare preceding abstracts).—The authors have developed theoretically a temperature formula for the calculation of the $E.M.F.$ of the Weston normal cell. This formula has the form:

$$E_t = E_0 + (E_0 + U_0/nFT_0)(T - T_0) - 1/2nFT_0(dU/dT)_0(T - T_0)^2 + 1/6nFT_0[1/T_0(dU/dT)_0 - (d^2U/dT^2)_0](T - T_0)^3 + \ldots$$

This formula is based on the Gibbs-von Helmholtz formula, $E = U/nF + T_0dE/dT$, and all symbols have their usual significance. The mechanism of the Weston element and data for the evaluation of $U_0, (dU/dT)_0$ and $(d^2U/dT^2)_0$ is obtained. The value of U_0 is found to be 47561 cal. $(dU/dT)_0 = 27{\cdot}10$ cal./degree, 18·64 and 17·44 cal. respectively when the various data available are employed in its calculation. The authors have therefore redetermined this data, and have obtained the following values: specific heat of mercury at 20°, 0·03338; molecular heat at 20°, 6·697; specific heat of $CdSO_4\frac{8}{3}H_2O$ at 20°,$\frac{8}{3}$0·2008; molecular heat at 20°, 51·50; specific heat of mercurous sulphate, 18·5—22·5°, 0·06400; molecular heat, 31·83; specific heat of $ZnSO_4,7H_2O$, 18·5—22·5°, 0·3184; molecular heat, 91·55. Calculating the value of $(dU/dT)_0$ from this data, the figure 22·38 cal./degree is obtained. The data presented indicate that the temperature formula of von Steinwehr (A., 1914, ii, 622) does not represent the facts.

J. F. S.

Electromotive Properties of certain Binary Alloys. III. Electromotive Behaviour of Cadmium-Antimony Alloys. ROBERT KREMANN and JULIUS GMACHL-PAMMER (*Int. Zeitsch. Metal.*, 1920, **12**, 241—245; from *Chem. Zentr.*, 1921, i, 123. Compare this vol., ii, 10, 11).—A series of cells composed of cadmium, normal cadmium sulphate solution, and cadmium–antimony alloys of varying composition has been examined in the manner described previously. The initial and final potential did not exhibit any marked differences. Slowly cooled alloys showed a slight rise in potential (about 20 millivolts nobler than cadmium) at 40 atom. % of antimony, due to the unstable compound, Cd_3Sb_2; this potential increases between 90 and 100 atom. % of antimony to that of the latter metal. Quenched alloys, on the other hand, exhibit a more definite increase in potential (about 150 millivolts) at 50 atom. % of antimony, caused by the stable compound, CdSb; this potential remains practically constant for alloys which do not contain more

than 90% of antimony. The surprising result that the stable equilibrium is set up in quenched, the unstable in slowly cooled, alloys, is confirmed by metallographic investigation. Kurnakov and Konstantinov find that stable equilibria are only attained by seeding or vigorous agitation; quenching is accompanied by violent mechanical shock. H. W.

Electromotive Properties of certain Binary Alloys. IV. Electromotive Behaviour of Alloys of Thallium with Zinc, Lead, Bismuth, Tin, Antimony, and Cadmium. ROBERT KREMANN and ALBERT LOBINGER (*Int. Zeitsch. Metallog.*, 1920, **12**, 246—256; from *Chem. Zentr.*, 1921, i, 123—124. Compare preceding abstract).—In the cells, Zn | *N*-zinc sulphate solution | $Zn_{(1-x)}Tl_x$, the potential of zinc is observed with alloys containing up to about 95 atom. % of thallium; the initial and final potentials are almost identical. In the series, Tl | thallous chloride solution saturated at 15° | $Tl_{(1-x)}Pb_x$, the potentials from 0 to 20 atom. % of lead are practically equal to those of thallium; from 50 to 100 atom. % of lead they are equal to the lead potentials; between 20 and 50 atom. % of lead the potentials pass into one another asymptotically. The final values, which are otherwise identical with the initial potentials, show a marked rise in the case of the alloys of very high lead content which is attributed to the formation of layers of oxide. In the series, Tl | thallous chloride solution saturated at 15° | $Tl_{(1-x)}Bi_x$, the initial potential of the alloys diminishes continuously from 0 to 25 atom. % of bismuth in conformity with the equilibrium diagram, then remains almost constant to 58 atom. % of bismuth, subsequently diminishes rapidly to 61 atom. %, and then remains almost constant to pure bismuth. The two compounds, $BiTl_3$ and Bi_5Tl_3, are relatively little less noble than thallium (about 50 and 140 millivolts respectively), and much less noble than bismuth (about 250 and 340 millivolts respectively). The initial potential of the cells, Tl | thallous chloride solution saturated at 15° | $Th_{(1-x)}Sn_x$, remains practically constant from 0 to 90 atm. % of tin, and then falls continuously to the value of the latter metal. Re-examination of the diagram of Kurnakov and Puschin indicates that tin scarcely forms mixed crystals with thallium, whilst the latter only does so with, at the most, 40 atom. % of tin. The thallium potential is shown by the series, Tl | thallous chloride solution saturated at 15° | $Tl_{(1-x)}Sb_x$, to 80 atom. % of antimony; the value then diminishes slowly at first, rapidly with more than 99 atom. % of antimony, to the potential of the latter. Electromotive evidence of the existence of the compound, $SbTl_3$, is not observed. In conformity with the equilibrium diagram, examination of the system Tl | electrolyte | $Cd_{(1-x)}Tl_x$, did not give any indication of the formation of a compound, the potentials corresponding closely with those of tin. Thallous chloride solution saturated at 15° and shaken with cadmium turnings and *N*-cadmium sulphate solution agitated with thallium turnings were used as electrolyte. H. W.

Electromotive Properties of certain Binary Alloys. V. Electromotive Behaviour of Tin–Sodium Alloys. R. KREMANN and JULIUS GMACHL-PAMMER (*Int. Zeitsch. Metal.*, 1920, **12**, 257—262; from *Chem. Zentr.*, 1921, i, 124. Compare preceding abstract).—The authors have investigated the series $Sn \mid 0{\cdot}1N$-sodium iodide solution in pyridine $\mid Sn_xNa_{(1-x)}$ and also in the cases of alloys containing less than 67 atom. % of sodium, the cells $Sn \mid N$-sodium sulphate solution in water $\mid Sn_xNa_{(1-x)}$. The existence of four compounds, Na_4Sn, Na_2Sn, $NaSn$, and $NaSn_2$ is indicated electromotively, but the presence of Na_4Sn_3 could not be detected. $NaSn_2$ is at least 980, NaSn at least 1080, millivolts less noble than tin. Na_2Sn and Na_4Sn are 520 and 240 millivolts nobler than sodium. H. W.

The Theory of Electrolytic Ions. XIX. Determination of the Size of the Benzene Nucleus from [Electrical] Conductivity. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1920, **113**, 131—134. Compare A., 1920, i, 897).—The radius of an ion and its mobility at 25° are connected by the expression $\rho = 1/v_{25} \times 89{\cdot}54 \times 10^{-8}$; making use of this expression, the authors have calculated the ionic radii of the various anions of the substituted arsinic acids from data previously published (A., 1919, i, 777, 897). It is found that the univalent ions have about the same radius, $3{\cdot}83 \times 10^{-8}$ cm., the bivalent $4{\cdot}40 \times 10^{-8}$, the tervalent $4{\cdot}68 \times 10^{-8}$ cm., whilst the *p*-phenylenediarsinic ion has a radius $7{\cdot}0 \times 10^{-8}$ cm. From these figures, it is concluded that the value $6{\cdot}2 \times 10^{-8}$ cm. found by Debye is too large for the radius of the benzene nucleus, whilst $1{\cdot}45 \times 10^{-8}$ found by Fajans (A., 1920, ii, 355) is too small. J. F. S.

Theory of Electrolytic Ions. XX. Hertz's Theory of Ionic Mobility. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1920, **113**, 135—140. See preceding abstract).—A theoretical paper in which the constants A and A' of Hertz's theory of ionic conductivity (A., 1912, ii, 120) are numerically evaluated and brought into a suitable form for general use. These have the form $A' = 167{\cdot}7/T^3 \times 10^9$, and since $A = \sqrt[3]{A'}$, $A = 5515/T$. An expression has been evolved for multivalent ions, and this has the form $A' = v^6 . 167{\cdot}7/T^3 \times 10^9$ and $A = v^2 5515/T$, where v is the valency. The relationship between the ionic mobility and the conductivity is discussed, and it is shown that only when the conductivity is regarded as a function of the concentration can a Hertz curve be constructed if the A constant is regarded as a universal constant, as is demanded by the theory. J. F. S.

The Theory of Electrolytic Ions. XXI. A First Proof of Hertz's Theory of Conductivity. RICHARD LORENZ and PHILIPP OSSWALD (*Zeitsch. anorg. Chem.*, 1920, **114**, 209—233).—The conductivities of aqueous solutions of sodium acetate were determined with an accuracy of 0·1%. From the numerous

points on the curve of conductivity plotted against concentration, it was possible to test the empirical laws of extrapolation to infinite dilution and the law of Hertz (A., 1912, ii, 120). The two empirical equations of Kohlrausch were found to break down, but the results agreed extremely well with Hertz's theory. The values at infinite dilution for sodium acetate were calculated as: 10°, $\mu_0=63\cdot15$; 18°, $\mu_0=76\cdot56$; 25°, $\mu_0=90\cdot05$. The absolute value of the universal constant in Hertz's formula was not confirmed, although its change with temperature agreed approximately with the theory. The constant is not universal, but must be found for each electrolyte. J. R. P.

Accurate Measurement of the Electrical Conductivity of Electrolytes at Temperatures up to 1600°. F. M. Jaeger and B. Kapma (*Zeitsch. anorg. Chem.*, 1920, **113**, 27—58).—The authors have described a method for the determination of the electrical conductivity of molten salts which may be used up to 1600°. An electric tube furnace is employed for obtaining the required temperature, which may be kept constant to 0·1°. Temperature measurements are made by means of a platinum–platinum-rhodium thermo-element, which is placed exactly in the centre of the melted salt. The electrode vessel is a small platinum tube with a rounded bottom (35 mm. diam. and 10 mm. high), which is suspended in the tube furnace by three platinum wires 1·5 mm. diam. The crucible itself constitutes one electrode, and the other is a similar vessel of 10 mm. diameter. The platinum used must be absolutely free from iridium. Full details are given for the determination of the cell constant, and all precautions necessary in the measurements are fully described. The following salts have been measured over the temperature range indicated, and the molecular conductivity is given in tables, which are reduced to a general formula in each case, by means of which the molecular conductivity may be calculated for any temperature. Potassium nitrate (346·1—500·4°), $\mu_t=36\cdot21+0\cdot1875(t-350)$; sodium nitrate (321·5—487·3°), $\mu_t=41\cdot56+0\cdot205(t-300)$; lithium nitrate (272·0—440·6°), $\mu_t=41\cdot14-0\cdot238(t-300)$; rubidium nitrate (318·8—493°), $\mu_t=33\cdot51+0\cdot145(t-300)$; cæsium nitrate (446·6—556·3°), $\mu_t=42\cdot13+0\cdot120(t-450)$; potassium fluoride (863·0—975°), $\mu_t=101\cdot8+0\cdot3163(t-900)$; potassium chloride (775·7—943·5°), $\mu_t=115\cdot4+0\cdot2575(t-800)$; potassium bromide (745·2—868·6°), $\mu_t=90\cdot09+0\cdot1906(t-750)$; potassium iodide (691·5—814°), $\mu_t=85\cdot41+0\cdot1564(t-700)$; sodium molybdate (843—1408°), $\mu_t = 107\cdot50+0\cdot183(t-850)$; sodium tungstate (752·5—1501°), $\mu_t = 83\cdot50+0\cdot185(t-750)$. The experimental values are compared with those calculated by the formulæ, and in every case there is a good agreement. J. F. S.

The Determination of Conductivity of Electrolytes by means of an Alternating Current Galvanometer. A. H. W. Aten (*Chem. Weekblad*, 1921, **18**, 51—52).—An investigation of

the suitability of the alternating-current galvanometer of Leeds and Northrup for the determination of conductivity by the Kohlrausch method. With sufficiently high resistances, and with platinised electrodes of sufficient surface, an accuracy of 0·3% can readily be obtained. The apparatus is suitable for various technical purposes, and can be arranged to give continuous automatic records. S. I. L.

Connexion between the Limiting [Electrical] Conductivity λ_∞ of Binary Electrolytes in Non-aqueous Solvents and the Viscosity η_∞ of the Latter: $\lambda_\infty \cdot \eta_\infty$ = Constant. P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, **113**, 85—97).—From a consideration of a large amount of data previously published by the author and others, and a small amount of new data, it is shown that the product $\lambda_\infty \cdot \eta_\infty$ =constant for a large number of acids and some salts in non-aqueous solvents. This rule holds for mixtures of solvents as well as for individual solvents. Water also obeys this rule when mixtures of solvents poor in water are considered, and when aqueous solutions of electrolytes with highly complex ions are considered. The temperature-coefficients of the viscosity and the limiting conductivity are practically identical, that is, $1/\lambda_\infty \cdot d\lambda_\infty/dt = -1/\eta_\infty \cdot d\eta_\infty/dt$, or the empirical rule $\lambda_\infty \cdot \eta_\infty$ =constant is independent of the temperature and the nature of the solvent over the temperature range 0—50°. The absolute value of $\lambda_\infty \cdot \eta_\infty = k$ depends on the nature of the electrolyte, and in the case of binary electrolytes varies between 0·5 and 1·0. Variations from the rule are found in solvents which have a high viscosity or which show a high molecular association; in these cases, the molecules of the solvent are relatively large, and will change their size with changes of temperature or concentration, and thereby change the degree of solvation of the electrolytes. To such solvents are to be numbered glycerol, ethylene glycol, formamide, and mixtures of these with water, sulphur dioxide, and ammonia. J. F. S.

Ionisation of Strong Electrolytes. WILLIAM D. HARKINS (*Proc. Nat. Acad. Sci.*, 1920, **6**, 601—605).—A discussion of the significance to be attached to the terms ion, ionisation, and dissociation. The author suggests that, to avoid confusion of ideas, the word ion should only be used for the charged particles which are free to move under a potential difference, and that for particles, which are not free to move, to which the term ion has also been applied by Sutherland, Milner, and Ghosh, the term polar atom should be used. Ghosh and others maintain that all strong electrolytes are completely ionised in solution, and for this condition the author suggests that the term ionisation be reserved, although it is not implied that the whole of the charged particles are free to move. For the other conceptions, the terms electrolytically dissociated and thermodynamically dissociated should be applied. J. F. S.

Dissociation of Ternary Electrolytes. C. DRUCKER (*Zeitsch. physikal. Chem.*, 1920, **96**, 381—427. Compare A., 1905, ii, 371; 1911, ii, 687; 1913, ii, 1015).—The dissociation relationships of sulphuric acid, oxalic acid, and tartaric acid, and the normal and hydrogen salts of these acids with thallium and potassium, have been investigated. The ionic concentrations were obtained either by *E.M.F.* measurements, cryoscopic measurements, or by conductivity measurements. It is shown that dilute solutions of concentration below 0·04*N* follow the law of mass action, and this occurs in certain cases also at higher concentrations. In some cases, a qualitative proof of the presence of complex ions is obtained. It is shown that the ionic conductivity of the primary ion of dibasic acids may be calculated by means of the formula of the type

$$\mu c = a\lambda_{Tl} + s\lambda_{SO_4} + s_a\lambda_{TlSO_4},$$

where μ is the molecular conductivity, c the concentration, λ_{Tl}, λ_{SO_4} and λ_{TlSO_4} the mobilities of the ions named, a the concentration of Tl', s that of SO_4'', and s_a that of $TlSO_4'$. Using this type of formula, the conductivity values of salts of the type Na_2SO_4 may be employed in the investigation of the dissociation of such salts, and in such cases it is found that in both dissociations the dilution law is followed. In all such cases, it therefore follows that the introduction of correcting factors into the dilution law are unnecessary. J. F. S.

Theoretical Considerations Concerning the Diamagnetism of Monatomic Gases. W. PAULI, jun. (*Zeitsch. Physik*, 1920, **2**, 201—205).—Debye has shown (A., 1920, ii, 356) that the cohesive force of a gas, an expression due to van der Waals, can be determined from the dielectric constant of the gas and certain principal electric moments of the molecules or atoms of the gas. The value of the cohesive force can, moreover, be calculated either from the value of a in van der Waals's equation for the gas, or from the temperature-coefficient of viscosity of the gas. Following the method of Langevin, the author shows that the magnetic moment of the atom of a monatomic gas can be expressed in terms of the moments referred to, and deduces the relation $\chi_A = 5{\cdot}96 \times 10^{19}\theta$, for the atomic diamagnetism χ_A of a monatomic gas, where $\theta = \frac{2}{3}\Sigma er^2$, r being the distance of the electron from the axis of the external field passing through the atomic nucleus. Corrected experimental values for the atomic magnetic susceptibilities χ_A of helium and argon give $\chi_A = 4{\cdot}6 \times 10^{-5}$ for helium, and χ_A for argon $= 25{\cdot}2 \times 10^{-5}$ or $23{\cdot}3 \times 10^{-5}$. These values lead to a value of θ for helium equal to $7{\cdot}7 \times 10^{-25}$ and for argon equal to 42×10^{-25} or 39×10^{-25}. Assuming atomic dimensions to be of the order 10^{-8}, these values are much larger than those to be anticipated from the kinetic theory. The observed susceptibilities of helium and argon are at least ten times larger than those anticipated from theoretical considerations. J. S. G. T.

Action of Light on the Thermal Conductivity of Selenium. BIANCA NANNEI (*Nuovo Cim.*, 1920, [iv], **20**, ii, 185—200).—The results of the author's measurements show that the thermal conductivity of crystallised selenium is increased by the action of light, but to an extent apparently less than is shown with the electrical conductivity. This effect seems to diminish as the temperature rises. T. H. P.

The Problems of Temperature Radiation of Gases MEGH NAD SAHA (*Phil. Mag.*, 1921, [vi], **41**, 267—278).—The results of King (*Astrophys. J.*, vols. 28, 34, 35, 37) indicate that temperatures between 2000° and 3000° are necessary for the excitation of the characteristic line radiation of the alkalis, alkaline earths, thallium, iron, vanadium, etc. In general, it appears that the higher the ionisation potential of an element the greater the difficulty of exciting its line spectrum. On the basis of the theory of electronic orbits, and the quantum theory of radiation, as developed by Bohr, Planck, Sommerfeld, Paschen, and Rubinowicz, the electronic orbits are classified according to their respective rotational and radial quantum numbers. The intensity of a spectrum line depends on the products of the relative proportions of orbits in the initial and final states of the appropriate electrons and on the chance of changing from one orbit to another. An investigation of the statistical distribution of atoms into different possible stable orbits, when the gas is subjected to a thermal stimulus, shows that a very small concentration of radiant atoms suffices for the emission of the lines of the principal series of the element. Employing Paschen's notation, the lines $(2, p)-(m, d_i)$, $(2, s)-(m, p)$, $(3, d)-(m, f)$ require gradually increasing concentrations of radiant matter. The following are respectively the temperatures of complete ionisation, temperature at which luminescence appears, and the temperature of maximum luminescence in the case of the respective elements: H, 24000°, 5000°, 12000°; He, 32000°, 11000°, 17000°; Mg, 24000°, 7500°, 11000°; Ca, Sr, Ba, 8000—10000°, 1500°, 4000°. The theory is applied to the phenomena of the reversal of spectral lines by absorption, and affords an explanation of the phenomenon observed by Wood and others, that in the case of sodium vapour, only the lines of the principal series are reversed. Reversal of the lines $(2, p)-(m, d)$ would occur at higher temperatures, and the lines of the Bergmann series, $(3, d)-(4, b)$, would be reversed at still higher temperatures. Such reversal of the Bergmann series should take place in the case of the alkali metals at 2000—3000°. J. S. G. T.

Thermodynamics of Mixtures. IV. MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **96**, 287—311. Compare A., 1920, ii, 596, 597).—A mathematical paper in which, among other things, it is shown that the assumption of Nernst ("Grundlagen des neuen Wärmesatzes," 1918, p. 157) that the drop in the specific heat of a given mass of a gas occurs earlier the greater the density, is a

natural consequence of his first assumption that every gas which is cooled at constant volume without condensation eventually reaches a condition of vanishingly small heat capacity. J. F. S.

Chemical Constants and Critical Data. FR. A. HENGLEIN (*Zeitsch. anorg. Chem.*, 1920, **114**, 234—240).—The chemical constant is calculated by the equation $C=\lambda_0/4{\cdot}571T$, where $\lambda=(\lambda_0+AT-BT^2-\ldots)(1-p/p_k)$ is the latent heat and p_k, T_k the critical constants. Nernst's equation, $C=0{\cdot}14\lambda/T_B$, where T_B is the absolute boiling point, follows from van der Waals's equation, $\log p/p_k=a(1-T_k/T)$. Cederberg's equation, $C=k\log p_k$ (where k is 1·6 in many cases) also follows from this equation, since it is a special case of the more general equation, $C=1{\cdot}1\log p_k/(T_k/T_B-1)$. The formula $\log p(\text{atm.})=-2642/T+2{\cdot}5\log T-0{\cdot}012175T+8{\cdot}474\times10^{-6}T^2-1{\cdot}3325\times10^{-9}T^3+4{\cdot}08355$ holds for water from 0° to the critical point; for oxygen the equation $\log p(\text{atm.})=-438{\cdot}8/T+2{\cdot}5\log T-0{\cdot}33752T+1{\cdot}223\times10^{-6}T^2-4{\cdot}0085\times10^{-7}T^3+2{\cdot}84387$ is deduced. J. R. P.

Critical Data and Valency in Organic Compounds. W. HERZ (*Zeitsch. anorg. Chem.*, 1920, **114**, 153—156).—It has been shown in previous papers (A., 1920, ii, 285, 414) that, if T_k, p_k, v_k represent critical temperature, pressure, and volume respectively, and z the sum of the valencies of the atoms contained in the molecule, $T_k/p_k\,.\,z=0{\cdot}44$ and $v_k/z=0{\cdot}00044$. From this it follows that $v_k\,.\,p_k/T_k=1\,.\,10^{-3}$, a relation which is now shown to hold with a fair degree of approximation for a number of organic compounds, principally aliphatic esters. It was shown in the papers referred to that, in the aromatic compounds, the value of the quotient $T_k/p_k\,.\,z$ tended to be low, about 0·37, instead of 0·44, the mean value, whilst in many aliphatic compounds it was nearer 0·49. It is now shown that if the ring carbon atoms in aromatic hydrocarbons are assumed to be tervalent instead of quadrivalent, the value of the above quotient for these hydrocarbons is increased to about 0·49, corresponding closely with the value for aliphatic compounds. This may have some significance in view of the supposed relationship between the structure of aromatic compounds and the crystal structure of graphite as determined by means of X-rays. E. H. R.

Theorem of Corresponding State and the Quantum Theory of Gases and Liquids. A. BYK (*Physikal. Zeitsch.*, 1921, **22**, 15—20).—A theoretical paper, in which the quantum theorem is applied mathematically to the theorem of corresponding state, and an expression is evolved which represents the whole of the physical thermodynamics of the liquid state. J. F. S.

Approximate Calculation of the Latent Heat of Fusion of the Liquefied Inactive Gases. J. NARBUTT (*Physikal. Zeitsch.*, 1921, **22**, 52—53).—The expression $A\rho/\theta=$constant for the elements of any given sub-group has been used to calculate the

latent heat of fusion of the inactive gases. The constant in the present case has been calculated from the experimental determination of the latent heat of fusion of argon (Eucken, *Beibl. Ann. Phys.*, 1916, **40**, 322), which has the value 0·268, $A\rho$ is the latent heat of fusion in Cals., and θ the melting point in degrees absolute. In this group the constant therefore has the value 0·0032. The following values in Calories have been obtained for the latent heat of fusion: helium, <0·004; neon, 0·08; argon, 0·268; krypton, 0·33; xenon, 0·43; and niton, 0·65. J. F. S.

Influence of Surface Tension on Fusion and Solidification. ERNST RIE (*Wien. Anz.*, 1920, 137—139; from *Chem Zentr.*, 1920, iii, 868).—In connexion with a communication by Pavlov (A., 1909, ii, 19) the author develops an expression for the dependence of the melting point, T_2, of small, crystalline granules on the surface tension, S_{23} (free energy of the surface), in the form $T_p - T_0 = -T_0 \times 2S_{23}/s_3rq$, where T_0 is the limiting melting point (without reference to surface energy), s_3 the density of the solid phase, r the radius of the crystalline granules considered as spheres, and q the latent heat of fusion. This expression, which is derived from the Gibb's equilibrium conditions by purely thermodynamic reasoning, and is readily adapted to the case of a drop enclosed within a crystal, gives results differing from those of Pavlov. Further observations of the melting points of crystals are necessary to decide which of the conditions, $S_{13} \gtreqless S_{12} + S_{23}$, is valid. Probably, the majority of amorphous substances are composed of extremely minute crystals, the size of the granules being $<10^{-5}$ cm.; the absence of a definite melting point is to be ascribed to surface tensions. H. W.

A Simple Method for the Determination of Melting Points and Critical Temperatures. HERMANN RASSOW (*Zeitsch. anorg. Chem.*, 1920, **114**, 117—150).—An apparatus was devised for melting-point determinations consisting of a solid cylinder of copper 10 cm. long and 5 cm. in diameter bored with an axial hole to a short distance below the centre for taking the specimen, a parallel hole for a thermo-couple, and a transverse hole intersecting the first hole at the centre of the cylinder. Through the transverse hole the specimen, illuminated by a lamp placed opposite the other end, was viewed through a telescope. The cylinder was heated electrically by a winding of nickel wire. The substance to be examined was sealed up in a tube of hard glass or transparent quartz, which was suspended through the axial hole in the field of view of the telescope. With this apparatus temperatures up to 1080° could be obtained with a limit of error ±1°. The following melting points were determined: potassium iodide, 684·1°; potassium cyanide, 601·2°; ammonium chloride, 519·7°; ammonium bromide, 541·9°; ammonium iodide, 551±3°, the accuracy being interfered with by dissociation; tetramethylammonium chloride, 420°±10°, much dissociation occurring; arsenic, 818°. Experiments were also made

on the melting points of mixtures of ammonium chloride with haloids of alkali metals. The method is not suitable for the determination of complete melting-point diagrams of mixtures, but serves to indicate whether miscibility of two salts is possible or not. With a quartz manometer on the principle of the Bourdon spiral, a determination of the vapour pressure of ammonium chloride between 340° and 520° was made. At 520° the vapour pressure is 37·5 atmospheres.

The melting-point apparatus was also used for the determination of some critical temperatures. The results obtained were: mercuric chloride, 704°; mercuric bromide, 738°; mercuric iodide, 797°; sulphur, 1040°; iodine, 553°. The critical temperatures of arsenic and mercury are above 1400°. E. H. R.

Vapour Pressure. LÉON SCHAMES (*Zeitsch. Physik*, 1920, **1**, 198—203).—A theoretical paper, in which certain problems in connexion with vapour pressure are mathematically discussed, particularly those relating to the latent heats and the chemical constants. J. F. S.

The Vapour Pressure and Sublimation Curves for some Important Metals. J. A. M. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1920, **114**, 105—116).—The formulæ deduced in a previous paper (A., 1920, ii, 588) are made use of in discussing the vapour pressures and sublimation pressures of the metals tungsten, platinum, molybdenum, copper, tin, lead, zinc, silver, bismuth, cadmium, antimony, and gold. E. H. R.

Distillation Apparatus for Small Quantities of Liquid. CARL WOYTACEK (*Chem. Zeit.*, 1921, **45**, 82).—The apparatus consists of a conical flask of 100 c.c. capacity and a small double-surface condenser attached vertically to the flask by a ground-in joint; the exit tube for the condensed vapours is near the lower end of the condenser. W. P. S.

Breaking of Halogen Bonds. A. VON WEINBERG (*Zeitsch. Physik*, 1920, **3**, 337—342).—By means of the expression $Q_{[M-Hal]} = a+b+c-d+Q_{[M]}+Q_{H-Hal}-\frac{1}{2}Q_{H}$, in which a is the heat of reaction of the solid metal [M] with water, b the heat of solution of the hydrogen haloid, c the heat of neutralisation, d the heat of solution of the salt, and Q the work of dissociation into atoms, the heat of dissociation of many halogen salts has been calculated. The following values of $Q_{[M-Ha]}$ have been obtained: LiCl, 193·2; NaCl, 181·4; KCl, 183·9; RbCl, 183·8; CsCl, 184·2; LiBr, 150·1; NaBr, 140·1; KBr, 144·2; RbBr, 145·0; CsBr, 145·8; LiI, 129·0; NaI, 120·9; KI, 126·6; RbI, 127·9; and CsI, 129·8. If the heat of sublimation is known, the work of dissociation of the compounds in the gaseous condition may be calculated. The heat of sublimation has been calculated, and the following values obtained: NaCl, 48·8; NaBr, 45·7; NaI, 43·3; KCl, 48·2; KBr, 45·2; KI, 44·9; and the

energy of dissociation of the vapours found to be: NaCl, 132·6; NaBr, 94·4; NaI, 77·6; KCl, 135·7; KBr, 99·0; and KI, 81·7.

J. F. S.

Volume and Heat of Hydration of the Ions. M. BORN (*Zeitsch. Physik*, 1920, **1**, 45—48. Compare A., 1919, ii, 204; Fajans, A., 1920, ii, 154).—In a previous paper Fajans (*loc. cit.*) has calculated the heat of hydration of certain ions on the basis of the author's formula for the lattice energy of binary salts (*loc. cit.*). The author now shows that the values put forward by Fajans are too large by about 100 Cals. in the case of the kations and too small in the case of the anions by about the same amount. A simple method of deducing the heat of hydration, W, is given, and the formula $W=\frac{1}{2}(1-1/\epsilon)N\,.\,2388\times10^{-11}e^2z^2/r_i$ Cals. deduced, in which N is the Avogadro number, z the valency, e the charge, and r_i the radius of the ion, and ϵ the dielectric constant of the solvent. Inserting the values for water as solvent, $W=1{\cdot}64\times10^{-6}z^2/r_i$ Cal. Using this equation, the following values of W are calculated: $H^{\cdot}$, 262; $Li^{\cdot}$, 110; $Na^{\cdot}$, 103; $K^{\cdot}$, 82, $Rb^{\cdot}$, 78; $Cs^{\cdot}$, 74; $Tl^{\cdot}$, 82; and $Ca^{\cdot\cdot}$, 344; Cl', 77; Br', 68; and I', 57. The values of r_i and r_a, the atomic radius, are also calculated, and it is shown that for positive ions $r_i<r_a$ and for negative ions $r_i>r_a$. The only exception to the above regularities among the elements examined is found in the case of thallium, where $r_i=2{\cdot}00\times10^{-8}$ and $r_a=1{\cdot}89\times10^{-8}$. If the above regularities are not due to chance, they indicate that the formation of a positive ion involves the removal of the outside electron of the atom, and in consequence the ion volume must be smaller than the atomic volume. The formation of a negative ion involves the absorption of an electron into the atomic structure, and consequently the ion has a larger volume than the atom.

J. F. S.

Heat of Mixture. H. CASSEL (*Zeitsch. Physik.*, 1920, **2**, 146—147).—The author advances a theoretical proof of the general validity of Dolezalek's principle discussed in a previous paper (A., 1920, ii, 664), namely, that every heat tone accompanying the mixture of condensed matter or every change of curvature in the vapour density isothermal is characteristic of a chemical reaction.

J. S. G. T.

Calculation of the Heat of Sublimation of the Alkali Haloids from the Lattice Structure. A. REIS (*Zeitsch. Physik*, 1920, **1**, 294—298).—On the basis of Born's method of calculating the ionisation energy from the atom ion lattice (A., 1919, ii, 204), the author has calculated the heat of sublimation of the alkali haloids. The following values are given: lithium chloride, bromide, and iodide, 15—35; sodium chloride, 58; sodium bromide, 55; sodium iodide, 51; potassium chloride, 52; potassium bromide, 50; potassium iodide, 46; rubidium chloride, 50; and cæsium chloride, 50. The present values are compared with those calcu-

lated by Haber (*Verh. Deut. Phys. Ges.*, 1919, **21**, 750), and a fairly good agreement found. J. F. S.

Dependence of the Heat of Vaporisation of Water on the Temperature. H. von Steinwehr (*Zeitsch. Physik*, 1920, **1**, 333—336).—A theoretical paper in which the author deduces an expression showing the dependence of the heat of vaporisation on the temperature, and the difference between the specific heats of the liquid and vapour. This expression has the form

$$r=[(dr/dT)_0-r_0/T_0]\{(1-aT_0)T\log_e T+aT^2\}+KT,$$

in which r is the heat of vaporisation per gram, T the absolute temperature of the process, and K a constant. The quantity, $dr/dT-r/T=h-s$, where h is the specific heat of the saturated vapour and s that of the liquid. Evaluating the constants and inserting them in the equation gives $r=-2\cdot098(1\cdot66776T\log_e T-1\cdot7874\times10^{-3}T^2)+20\cdot765$. The equation is tested by plotting the values of $dr/dT-r/T$ against T, when a straight-line curve is obtained, and the calculated values of r from 30·12° to 180·72° are compared with the experimental values of Henning (*Ann. Physique*, 1909, [iv], **29**, 441) for water, when a remarkably good agreement is found. J. F. S.

The Heat of Vaporisation of Water as a Function of the Temperature. F. Henning (*Zeitsch. Physik*, 1920, **2**, 197—199). —A simple thermodynamic proof is advanced of the result obtained by Steinwehr (preceding abstract) for the difference in the respective specific heats at constant pressure of water in the vapour and liquid states, the vapour pressure being small. Making certain assumptions, the relation deduced from a well-known thermodynamic relation takes the form $dr/dt=(c_p)_1-(c_p)_2$, where r is the latent heat of vaporisation at temperature $t°$, and $(c_p)_1$, $(c_p)_2$ the respective specific heats in the vapour and liquid states. The values of dr/dt deduced from experimental values of $(c_p)_1$ and $(c_p)_2$ are in close agreement with the experimental values of dr/dt, corresponding with 40° and 50°, found by the author. Values are tabulated in the original for the latent heat of vaporisation of water, r, at temperature $t°$, and for the temperature-coefficient thereof. J. S. G. T.

Molecular Attraction. V. K. K. Järvinen (*Zeitsch. physikal. Chem.*, 1920, **96**, 367—374. Compare A., 1920, ii, 165).—In a previous paper (*loc. cit.*), the author put forward the formula m^2k/r^n as an attraction law. This was applied to mercury with values of $r=5$ or 6, by means of which the value of the heat of vaporisation of mercury at 360° was calculated to 15,350 and 12,300 respectively. These values are not in keeping with the thermodynamic value, which lies between 13,810 and 14,490. Consequently, the author has now tested the formula $F=m^2k/r^{5\cdot5}$ in the case of mercury, and finds that the value $n=5\cdot5$ is in better accord with fact. The latent heat of fusion has been calculated from the change in volume by means of the formula

$W_s = ks_1^{1.5} - ks_2^{1.5}$, where s_1 and s_2 are the densities of the solid and liquid respectively. A moderate agreement is found between the calculated and experimental values in the case of sodium and potassium, but in other cases the two values are widely divergent.

J. F. S.

The Relative Volumes of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1921, **122**, 62—66).—The relative volume of CH_2 at 15° is 16·42. The relative volumes at 15° of the following elements or radicles are: Cl, 23·01; Br, 27; I, 32·75; NH_2, 16·42; CN, 23·96; N_3, 32·63; NO_2, 26·74; NO_3, 34·27; SH, 25·48; C_2H_3, 41·87; C_2H_2, 28·89; C_2H, 31·25; CO_2Me, 49·71; CO_2Et, 66·13; CO_2Pr, 82·55; $CO_2\cdot C_4H_9$, 98·97; $CO_2\cdot C_5H_{11}$, 115·39; C_6H_5, 77·48; C_6H_5, 74·45; OH, 13·29; OH, 10·21; CCl_3, 69·74; CO·OH, 23·8.

J. R. P.

The Molecular Volumes of the Alkali Haloids. K. FAJANS and H. GRIMM (*Zeitsch. Physik*, 1920, **2**, 299—308).—The values of the respective densities, molecular weights, molecular volumes, and coefficients of cubical expansion of the haloid salts of lithium, sodium, potassium, rubidium, and cæsium, as determined by various observers, are tabulated. It is shown that a linear relation of the form $y = \alpha x + a$ holds between the molecular volume, y, of one haloid salt and the corresponding value, x, of another haloid, the two salts containing a common kation or anion. This relation is exemplified by the relations $V_{Kx} = 1{\cdot}130V_{Nax} + 6{\cdot}95$, $V_{MBr} = 1{\cdot}070V_{MCl} + 3{\cdot}16$, $V_{Nax} = 1{\cdot}112V_{Lix} + 4{\cdot}25$. The values of α and a are tabulated in the case of all the haloid salts of the alkali metals, employing Baxter's values of the densities of lithium, sodium, potassium, and rubidium haloids. In the case of the fluorides of cæsium and rubidium, the respective molecular volumes are deduced from those of the fluorides of lithium, sodium, and potassium, assuming the above linear relation to hold. The respective molecular volumes so deduced are 29·1 cm.^{3} for cæsium fluoride and 28·8 cm.^{3} for rubidium fluoride at 25°. Whilst the atomic volume of cæsium, 71·0, is much larger than that of rubidium, 55·8, the molecular volumes of the iodide, bromide, and chloride of cæsium are smaller than the corresponding molecular volumes of the rubidium haloids. The question is raised as to whether the crystalline structure of the cæsium haloids is the same as that of the other alkali haloids. The difference between the molecular volumes of any two haloids containing either a common kation or anion increases with increase in the molecular volume of the common constituent. In the linear relation specified, the values of α and a increase together, except in the case of the cæsium salts. On the basis of the hypothesis of Born, namely, that the outside electrons in the atoms are arranged along the edges of a cube, the distance between neighbouring, oppositely charged ions in the haloid salts is shown to be given by the relation $r = 0{\cdot}938 \times 10^{-8}\sqrt[3]{V}$ cm., where V is the molecular volume of the salt. The values of r are tabulated. It is pointed out

that the difference between the respective spheres of influence of two ions combined with a common ion decreases with increase in the molecular dimensions of the common constituent. The sphere of influence of an ion is not a sharply defined magnitude, but depends on the ions in the neighbourhood of the ion in question. The sphere of influence of an ion is not an additive quantity, even at absolute zero. J. S. G. T.

The Effect of Adsorbed Gases on the Surface Tension of Water. SHANTI SWARUPA BHATNAGAR (*J. Physical Chem.*, 1920, **24**, 716—735).—The disk method of measurement was used with a segment of a quartz sphere as the disk, a spring being used as a Joly's balance. The values for the surface tension of water in various gases at 15°, expressed as dynes, were: in a vacuum 71·3, in hydrogen 72·83, in nitrogen 73·00, in carbon monoxide 73·00, in carbon dioxide 72·85, in air 73·1. Excepting for carbon dioxide, the increase in value of T for water in gases is proportional to the rise in their densities. Stöckle and Meyer's data for the values of T for mercury show a similar discrepancy with carbon dioxide (compare Freundlich, "Kapillarchemie," 1909, 86). W. G.

The Use of Silica Gel as an Adsorbent for Vapours. E. B. MILLER (*Chem. and Met. Eng.*, 1920, **23**, 1155—1158, 1219—1222, 1251—1254).—Special characteristics of the silica gel which render it adaptable to the adsorption of vapours are its easy preparation by coagulation of a colloidal solution of silicic acid, uniform reproduction, and its inertness and stability at even high temperatures. Its use was therefore tested in investigations on adsorption phenomena. The fact that vapours of liquids of high boiling point are more readily adsorbed, and that adsorption decreases with increasing temperature but increases with the partial pressure of the vapour, suggest that condensation of the vapour in the adsorbent takes place. Factors which influence adsorption are the ratio of the partial pressure of the vapour, P, to its vapour pressure at the temperature of adsorption, P_0, this ratio, P/P_0, being termed the "corresponding pressure," and the compressibility of the adsorbed liquid; to secure activity of the adsorbent, its internal volume must be as large as possible, and made up of spaces of minimum dimension. Increase of temperature reduces adsorption, whilst increase of concentration improves it. Recovery of adsorbed vapours is effected by raising the temperature of the gel, or by decreasing the partial pressure of the vapours, either by exhaustion or by displacement with air, steam, or other gas. Laboratory scale experiments were carried out with mixtures of air and sulphur dioxide, ether, acetone, benzene, light petroleum, and water vapour; the saturation values and efficiency of adsorption from given concentrations are tabulated and plotted on curves, and the yields of recovered vapour are given in each case. [See *J. Soc. Chem. Ind.*, 1921, Mar.] W. J. W.

Calculation of the Diffusion Constant of Dissolved Substances. HANS VON EULER and ARVID HEDELIUS (*Zeitsch. anorg. Chem.*, 1920, **113**, 59—68).—Experiments have been made to ascertain to what extent the presence of other substances influences the velocity of diffusion of a given substance, and a method is devised whereby the diffusion constant may be calculated in the case of moderately concentrated solutions. The method is expressed by the following rule. The diffusion constant of a solution of a given concentration obtained experimentally is multiplied by the coefficient of viscosity of a solution of one-fourth the concentration of the original solution and divided by the relative osmotic pressure of the dilute solution. Curves are given for the variation of the relative viscosity with concentration, and the relative osmotic pressure with concentration for solutions of sucrose of concentrations 0—1*N*.
J. F. S.

Hydro-diffusion of Magnesium Ammonium Sulphate and Separation of its Component Salts. C. PORLEZZA (*Gazzetta*, 1920, **50**, ii, 285—296).—The diffusion of magnesium ammonium sulphate solution has been investigated by means of the method and type of apparatus described by holm (A., 1905, ii, 147). The ammonium salt is found to diffuse more rapidly than the magnesium sulphate (compare Rüdorff, A., 1889, 98; Torrance and Knight, A., 1918, ii, 299). The numerical results obtained in experiments at 10° confirm the observation that the coefficients of diffusion of two salts diffusing together undergo diminution, the velocity of diffusion diminishing the more for the salt having the less coefficient of diffusion. Simple diffusion into water cannot effect complete separation of the two salts except by repeated diffusion of the diffusate. Better results should be obtainable by taking advantage of the fact that magnesium ammonium sulphate is only slightly soluble in presence of one of its components, so that concentration of a solution containing double salt and one component should lead to almost complete separation of the former. T. H. P.

Ionic Velocities in Non-aqueous Solutions. P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, **113**, 113—124).—A theoretical paper, in which from previously published data the author shows that the product of the ionic conductivity and the viscosity of the solvent is a constant quantity, $l_a \times \eta_\infty$ = const., and $l_c \times \eta_\infty$ = const. The velocities of the ions are inversely proportional to the viscosity of the solvent, and these products are independent of the temperature. It is also shown that the transport number at infinite dilution is practically the same as that at any other dilution for dilute solutions. For one and the same ion in different solvents the same transport number is obtained. Aqueous solutions of various ions with the exception of the hydrogen ion give the same transport numbers as non-aqueous solutions, and in general it may be said that in high dilutions with highly dissociated binary electrolytes the transport numbers of a given ion are independent of the nature

of the solvent and of the temperature. This is expressed by the equation $l_a \cdot \eta_\infty / (l_a \cdot \eta_\infty + l_c \eta_\infty) = n_a = \text{const.} k_1$. J. F. S.

Diameter of Ions in Non-aqueous Solutions. P. WALDEN (*Zeitsch. anorg. Chem.*, 1920, **113**, 125—130).—A theoretical paper, in which, by means of Einstein's formula, $U = K/N \cdot 6\pi\eta\rho$, in which U is the velocity of a particle, K the force acting on a particle, N the Avogadro number, η the coefficient of viscosity, and ρ the radius of the particle, the radius of a number of ions in methyl alcohol solution has been calculated. It is shown that for most ions the value of ρ lies between 2.0×10^{-8} cm. and 3.9×10^{-8} cm. Hydrogen has a smaller value, 1.1×10^{-8}, and lithium a larger value, 4.70×10^{-8} cm. The ionic radius in non-aqueous solvents follows the same order as in aqueous solutions, namely, $H^{\cdot} < K^{\cdot} < Ag^{\cdot} < Na^{\cdot} < Li^{\cdot}$ and $Br' < I' < Cl' < NO_3'$. In the case of the above-named simple ions the ionic radius in aqueous solutions and the atomic radius are practically the same except in the extreme cases hydrogen and lithium, whilst in non-aqueous solutions the values of the ionic radius are about twice as great. The mean values obtained are, in aqueous solution 2.67×10^{-8} cm., and in non-aqueous solution 5.33×10^{-8} cm. A further set of ions, consisting of organic anions and kations, has the same ionic radius in both aqueous and non-aqueous solutions, the mean value in this case being 4.4×10^{-8} cm. The difference in the radius in the case of the simpler ions is held to indicate a much greater solvation in non-aqueous solvents than in water. J. F. S.

Aqueous Solutions. OTTO PULVERMACHER (*Zeitsch. anorg. Chem.*, 1920, **113**, 141—148).—It is shown that the formula $\eta_x = Ax + 1$ represents the viscosity of aqueous solutions equally as well as the formula of Arrhenius $\eta_x = A^x$ (A., 1898, 336). In the case of mixed solutions the author puts forward the formula $\eta_{xy} = \eta_x + \eta_y - 1$ in place of the Arrhenius formula $\eta_{xy} = A^x \cdot B^y$. Both formulæ give equally good results, and in all cases except the most concentrated solutions are in keeping with the observed results. The author has determined, at 25°, the relative viscosity, the absolute fluidity (ψ), the density, d_4^{25} the specific volume, v, and the refractive index, n_D, for solutions of sodium chloride, ammonium sulphate, and mixtures of the two, magnesium sulphate, potassium sulphate, magnesium chloride, potassium chloride, and binary mixtures of these. It is shown that the viscosity may be calculated for the mixtures by the above-mentioned formula with fair accuracy, but, using the fluidity and the usual mixture rule as suggested by Bingham (A., 1909, ii, 382), much better agreement between calculated and experimental values is obtained. Similar determinations have been made with dextrose, galactose, maltose, lactose, and sucrose, and it is shown in connexion with these substances the equation $K = \sqrt[3]{\eta}/n_D^2 \cdot d^2$ obtains, but for solutions of electrolytes the value of K is not in the least constant. J. F. S.

Significance of Recrystallisation. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **113**, 163—178. Compare A., 1919, ii, 273).—The recrystallisation of metals when worked cold is discussed. It is known that when metals are worked cold or at temperatures much below the melting point large crystals are produced at the expense of the smaller crystals. The older distillation hypothesis put forward to explain the process is considered and shown to be incapable of successfully explaining it. The author puts forward a new hypothesis to explain the process, and considers a number of facts in connexion with recrystallisation from the point of view of this hypothesis, and in all cases finds it satisfactory. The hypothesis is as follows: Two contiguous crystals can only be in equilibrium with one another when the crystallographic equilibrium lattice planes of both crystals lie together in the same plane at the surface of contact, that is, when the space lattices of both crystals of the contiguous crystals form a single lattice or when the plane of contact is a twinning plane. If one or the other of these conditions is not fulfilled, then when the temperature is raised sufficiently to allow of a certain amount of change in the position of the atoms or molecules in the lattice, new lattices of mean orientation to the surface of contact will be formed, that is, a recrystallisation will commence. J. F. S.

Velocity of Migration of the Ions in Crystals. G. VON HEVESY (*Zeitsch. Physik*, 1920, **2**, 148—149).—Extraordinarily small values for the velocities of migration at the ordinary temperature of the ions in rock salt are deduced from the conductivity data of rock salt crystals by the application of the Einstein relation between diffusion and mobility. Thus in rock salt, the migration constant at 20° is about 3×10^{-18} cm.^{2} per day, about $1/10^{18}$ of that of the ions in the fused salt. The migration velocity increases rapidly with temperature, the migration "constant" in the case of rock salt attaining the value $1{\cdot}4 \times 10^{-5}$ cm.^{2} per day at 626°, about 1/3000 of that in the case of the fused salt. The migration velocities of the ions in crystals of lead chloride at a temperature 30° below the melting point of lead chloride have been determined by determining the rate of diffusion of radioactive lead chloride in a compressed mass of lead chloride crystals. The experimentally determined value of the migration constant at this temperature was 0·029 cm.^{2} per day, in satisfactory agreement with the value 0·027 cm.^{2} per day, calculated as above. The calculated value at the ordinary temperature is 8×10^{-8} cm.^{2} per day. The agreement between experimental and calculated results in the case of lead chloride suggests that the calculated values in the case of rock salt are probably correct. In mixed crystals, migration velocities are, as a rule, greater than in crystals of a pure substance. In all cases, mixed and pure crystals alike, the migration velocity begins to increase rapidly at a temperature in the neighbourhood of the melting point, which is in agreement with the conclusion reached by Tammann from other considerations. While this preliminary

to the process of fusion commences at a higher temperature in the case of the nitrates than in the case of the chlorides of the alkalis, the converse is the case with the haloids of the heavy metals.

J. S. G. T.

The Crystal Lattice. A. Reis (*Zeitsch. Physik*, 1920, **2**, 57—59).—In this appendix to his previous paper (A., 1920, ii, 537) dealing with the classification of the several points of the crystal space-lattice into natural groups, the author advances evidence supporting his statement that the classification can be effected from geometrical considerations. The following rules hold for the various natural-point groups of the lattice. (1) A connecting line between two natural point groups can never be crystallographically equivalent to a connecting line in the interior of a group. (2) The shortest connecting line between two natural point groups is longer than the longest connecting line necessary for the internal cohesion of a natural point group. (3) The natural point groups are those satisfying conditions (1) and (2). No natural point groups exist in the case of most of the space-lattices of the metals hitherto determined. Such space-lattices are termed atomic-ion lattices. To this class belong the lattices of the diamond, silicon, the alkali haloids, fluorite, and zinc blende. A second class of space-lattice is characterised by two atomic point groups. These are termed radicle-ion lattices, and are exemplified by the cases of calcite and pyrites. It is surmised that the silicates characterised by their hardness, and salts of similar complex acids—the titanates, borates, phosphates, niobates, tungstates, etc.—possess space lattices belonging to a third class, the honeycomb lattices. Spinel is probably the simplest representative of this class. J. S. G. T.

Phenomena in the Formation of Space Lattices Composed of Two Different Species of Atoms, particularly in the Formation of Mixed Crystals of Silver and Gold. G. Tammann (*Zeitsch. anorg. Chem.*, 1920, **114**, 281—288).—When the soluble component of a mixed crystal is removed, the atoms of the insoluble residue may behave in four ways: (1) remain as an atomic dust or conglomerate of particles with irregular atomic grouping; (2) combine to microscopic crystals; (3) combine with the solvent or solute, although the substance in mass is not attacked; (4) combine together and attract other atoms to the chain.

With mixed crystals of gold and silver (and probably other metals), case (2) only occurs on extraction with sulphuric or nitric acids. With mixed crystals of platinum with silver or copper, cases (2) and (3) occur simultaneously. The behaviour of alloys of platinum with lead, bismuth, or zinc, containing platinum compounds, is similar. Mixed crystals of iron with silicon on treatment with hydrochloric acid give only silicic acid. Silicon hydride is evolved when the silicon is in combination with an electropositive metal, such as magnesium, which forms Mg_2Si. Iron–carbon mixed crystals give hydrocarbons with hydrochloric acid.

The residue of gold left after dissolving out the silver from an alloy was found by X-ray examination to be crystalline, although it was finely divided and almost black. At higher temperatures, the particles are larger and yellow. The separation of gold and silver is described. The residue of silver in the gold after treatment with acid is appreciable when the original alloy contains only small quantities of silver, and increases as the amount of silver in the alloy decreases. The amount is not appreciably altered by tempering. J. R. P.

Size of the Ions and Lattice Energy of the Alkali Haloids. K. FAJANS and K. F. HERZFELD (*Zeitsch. Physik*, 1920, **2**, 309—331).—On Born's theory of lattice energy, in which the potential energy of the residual neutral parts of the ions is inversely proportional to the ninth power of the distance, it is found that the lattice energy of the sodium haloids is 9 Cal. per mol. too large, assuming that the values for the potassium haloids are correct. Modifying Born's formula for the potential energy by the introduction of terms containing the inverse fifth power and the inverse seventh power of the distance, in the case of kations and anions of different sizes, an equation is derived whereby the ionic radii may be determined in numerous cases. Applying the results to the case of the alkali haloids, the following values are obtained for the ionic radii of the respective alkali cations and haloid anions: Na, $0{\cdot}517 \times 10^{-8}$ cm.; K, $0{\cdot}794 \times 10^{-8}$ cm.; Rb, $0{\cdot}914 \times 10^{-8}$ cm.; F, $0{\cdot}75 \times 10^{-8}$ cm.; Cl, $0{\cdot}953 \times 10^{-8}$ cm.; Br, $1{\cdot}021 \times 10^{-8}$ cm.; I, $1{\cdot}122 \times 10^{-8}$ cm. The values calculated therefrom for the distances between the atoms of the respective haloids are in very close agreement with observed values. The calculated values for these distances are, in 10^{-8} cm.: NaF, 2·34; NaCl, 2·817; NaBr, 2·980; NaI, 3·231; KF, 2·67; KCl, 3·141; KBr, 3·295; KI, 3·527; RbCl, 3·286; RbBr, 3·440; RbI, 3·672. The ionic dimensions are substituted in an expression involving the inverse first, fifth, and seventh powers of the distance, and corrected values of the respective lattice energies of the several alkali haloids are derived. The values so calculated in Cals. per mol., are: NaF, 210·4; NaCl, 170·0; NaBr, 159·7; NaI, 146·7; KF, 192·2; KCl, 159·0; KBr, 150·4; KI, 139·1; RbCl, 154·6; RbBr, 146·5; RbI, 135·8. These values are in closer agreement with values derived from experimental data than any hitherto deduced. The theory developed removes the discrepancy in the relative magnitudes of the lattice energies of the respective sodium and potassium haloids, and, moreover, explains the smaller relative value of the repulsion potential, derived from available compressibility data connected with the alkali haloids, in the case of the sodium salts as compared with the potassium salts. J. S. G. T.

The Molecular Directing Force in Liquid Crystals. O. LEHMANN (*Zeitsch. anorg. Chem.*, 1920, **113**, 253—305).—A theoretical discussion of the properties of different kinds of fluid crystals, as revealed by their optical behaviour. The properties

are best accounted for on the assumption that the fluid crystals have a leaflet-like structure, the units of which endeavour, as far as possible, to remain parallel, but can glide freely in a direction parallel to their faces (compare following abstract). E. H. R.

The Molecular Forces Operative in Liquid Crystals and their Relation to Known Forces. O. LEHMANN (*Zeitsch. Physik*, 1920, **2**, 127—145).—A critical review of the theory of Groth concerning the forces operative in the production of crystalline structure. The author contends that, in general, the surface of a crystal surrounded by another medium is a surface of uniform surface tension, and the orientation of the molecules of liquid crystals is in no way conditioned by surface tension considerations. Departure from the spherical form normally assumed by a surface of uniform surface tension is illustrated by imagining the molecules to be built up of a number of flat wedges the alternate edges of which are parallel, the whole being enclosed within a uniformly taut elastic membrane. The wedges move freely on rollers. A laminar structure is produced by the penetration of one set of wedges into the space between neighbouring wedges in an adjacent row. The production of a laminar structure as the result of anisotropy of the impacts of the molecules, due to temperature, is shown to be untenable. An explanation of the tendency of the molecules of a liquid crystal to possess directional properties is afforded by considering the molecules as analogous to astatic magnetic systems. The molecules may, in like manner, be regarded as constituted of positive atoms placed at the corners of a cube, about which electronic orbits are executed alternately in counter-directions. Crystalline structure originates in the tendency of the laminar molecules to be arranged at equal intervals, and their capability of gliding parallel to their flat surfaces. The term "liquid crystals" applied to these substances is justified by their properties. J. S. G. T.

Measurement of Solvation (Swelling) in Colloids. H. LÜERS and M. SCHNEIDER (*Kolloid Zeitsch.*, 1921, **28**, 1—4). —The authors have made a comparative study of Hofmeister's weight method, Fischer's volume method, and Wo. Ostwald's viscosimetric method for the determination of the amount of swelling of colloids. The measurements include determinations of the increase in weight of gelatin in water, the change in the viscosity of gliadin in lactic acid of various concentrations, the sedimentation height of barley flour, and the change in the viscosity of suspensions of barley flour. The results show that the three methods named furnish similar results, are generally applicable, and trustworthy. J. F. S.

The Limiting Size of Colloidal Particles in a Brownian Motion. BUNSAKU ARAKATSU and MITSUHARU FUKUDA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 179—182).—Sols of the metals gold, silver, copper, cadmium, zinc, tin, magnesium, nickel, aluminium,

platinum, and tungsten, prepared by Bredig's method, were examined by measuring the diameter of the smallest particle which could be found in a state of rest. The limiting size, which appeared to be the same for all the metals, was approximately $2·6\ \mu$. In the case of cadmium, zinc, tin, and magnesium, the particles were all so small that no measurement could be effected. The effect of increasing the viscosity of the sol was examined by adding a concentrated solution of sugar or glycerol, measuring the viscosity, and then examining as before with the ultramicroscope. These experiments were made with gold and copper sols, and it was found in each case that by plotting the logarithm of the limiting size of the particle, a, against the viscosity, η, a straight line was obtained. For the gold sol, the relation can be expressed by $a\eta^{0·229}=3·5$, and for copper, $a\eta^{0·249}=3·4$. E. H. R.

Coagulation of Colloidal Solutions by Electrolytes: Influence of Concentration of Sol. E. F. BURTON and (MISS) E. BISHOP (*J. Physical Chem.*, 1920, **24**, 701—715).—The three aqueous colloidal solutions used were gum mastic sol, Bredig copper sol, and arsenious sulphide sol. The results show that the coagulative power of any given ion varies with the concentration of the disperse phase of the colloidal solution, as follows. For univalent ions, the concentration of ion necessary to produce coagulation increases with decreasing concentration of the colloid, this increase being very rapid with low concentrations of the colloid. For bivalent ions, the concentration of the ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid. For tervalent ions, the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

The authors suggest that there are at least two properties of the system, made up of colloidal solution plus electrolyte, which have influence in determining the coagulating power of any ion. These two influences are such that they tend to counteract one another to a certain extent. One of them dominates the action of univalent ions, whilst the other dominates the action of tervalent ions. In the action of bivalent ions, the two influences seem to be nearly equalised. W. G.

Gold Numbers of Electrolyte-free Fractions of Albumin from Normal and Immune Serums and their Sensitising Action on Colloidal Suspensions. JOSEPH REITSTÖTTER (*Kolloid Zeitsch.*, 1921, **28**, 20—24).—The gold number and the sensitising action of electrolyte-free albumin and paraglobulin on ferric hydroxide sols have been determined. The albumin fractions were prepared from the normal and immune serums of several animals by the electro-osmotic method. The albumins have the smallest gold number, and are followed in order by paraglobulin and euglobulin. It is shown that the gold number is not a characteristic constant in the case of anti-substances. Different antitoxic serums from the same type of animal have the

same gold number within the limits of the experimental accuracy, and different bactericidal serums have the same protective action toward colloidal gold as the normal serums. The gold number is independent of the nature of the serum. Different albumin fractions exhibit widely different sensitising actions on ferric hydroxide sols, but all albumin–ferric hydroxide sols are much more sensitive to electrolytes than the pure ferric hydroxide sols. Paraglobulin has a similar, but somewhat less marked, action than albumin. Paraglobulin antitoxic serums have a greater sensitising action than the normal or antibacterial serums, from which it is deduced that the specific anti-substances have a larger negative charge than the normal paraglobulin. It is possible to differentiate between paraglobulin and antitoxic serums by purely physico-chemical measurements without experiments on animals, and the sensitising action on ferric hydroxide sols may be regarded as a reaction for the anti-substances. J. F. S.

Three Phase Emulsions. H. BECHHOLD, L. DEDE, and L. REINER (*Kolloid Zeitsch.*, 1921, **28**, 6—19).—It is shown that pairs of immiscible liquids such as water–benzene and water–petroleum may be emulsified by shaking with alumina, zinc dust, or yeast. The emulsion formation depends on the size of the particles of the powder, its quantity, and on the addition of certain substances (emulsion promoters). The emulsifying power of the powder (emulsion former) increases to a maximum with decreasing size of the particles, and then decreases with a further decrease in the size of the particles; the more solid phase present the larger the amount of emulsion produced. The powder forms a sheath round the individual drops of the disperse phase, and prevents them coalescing, and consequently the greater the amount of powder the greater the surface which it can thus protect, and so the greater the amount of emulsion formed. The emulsion promoters must be soluble in one or both of the liquid phases. Benzene and water are not emulsified by shaking with alumina powder, but the addition of a few drops of such substances as pyridine, acetic acid, ethyl alcohol, sodium hydroxide, or sodium nitrate immediately causes emulsification. It is probable that the rôle of the emulsion promoter consists in some action influencing the wetting of the powder by the two liquid phases. The relative surface tension of the two liquids has no influence on the emulsification, and consequently the change of surface tension brought about by the emulsion promoter cannot have any effect on the emulsification. The systems named above have been examined, and the maximum quantity relationship for complete emulsification determined. It is shown that in general the maximum relationship lies between 60 to 80 volumes of the disperse phase to 20 to 40 of the dispersion medium. Theoretically, this relationship is deduced as 74:26. The volume of the emulsion is influenced by the density of the solid phase and that of both liquid phases. Large differences in the density bring about a diminution of the emulsion layer. J. F. S.

Influence of the Ionising Tension on Chemical Reactions in Gaseous Mixtures, particularly, in the case of the Inert Gases. FRANZ SKAUPY (*Zeitsch. Physik*, 1920, **1**, 49—50).—When freshly filled tubes of neon and argon are used for the first time the spectrum is always found to indicate the presence of carbon compounds. In the case of a neon tube the carbon spectrum vanishes in a few seconds, whilst in the case of an argon tube it persists for hours, but eventually disappears. The author explains the different behaviour as follows: the ionisation potential of carbon compounds lies between that of neon and argon, so that when the potential is applied to the neon tube the carbon compound takes up by preference the electrons, and is decomposed by them to form non-volatile derivatives, whilst with an argon tube the argon takes the electrons and the carbon compound is therefore only slowly destroyed. An analogous case is found in the purification of argon or neon from nitrogen by heating with a mixture of calcium chloride and carbide; in the latter case the reaction is much more rapid than in the former case. The explanation is similar to the foregoing explanation: the red hot calcium compounds emit electrons which ionise the nitrogen in preference to the neon; the nitrogen ions then react with the carbide, whilst in the other case they ionise the argon in preference to the nitrogen, and so the reaction is retarded. It would seem, therefore, that the inactive gases are capable of exerting an influence on the velocity of chemical reactions which are brought about by the presence of free ions. J. F. S.

Reversible Reactions of Carbon Monoxide on the Oxides of Iron. GEORGES CHAUDRON (*Compt. rend.*, 1921, **172**, 152—155).—Starting with ferric oxide and carbon monoxide, the author has studied the equilibria over a temperature range of 300—1000°. The ferric oxide is reduced to the magnetic oxide, and beyond this stage two reactions may occur. Below 580° there is a single system corresponding with the equation $Fe_3O_4 + 4CO \rightleftharpoons 4CO_2 + 3Fe$. Above 580° there are two equilibria before arriving at iron, namely, $Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$ and $FeO + CO \rightleftharpoons Fe + CO_2$. The three solid phases co-exist in equilibrium at 580°. Below 580° ferrous oxide is unstable, and is transformed into a mixture of iron and the magnetic oxide, $4FeO \rightleftharpoons Fe_3O_4 + Fe$. W. G.

Binary Equilibria with Solid Carbon Dioxide. A. THIEL and E. SCHULTE (*Zeitsch. physikal. Chem.*, 1920, **96**, 312—342).—The binary systems between solid carbon dioxide and ethyl ether, ethyl chloride, methyl ether, chlorine, hydrogen sulphide, and carbon disulphide have been investigated. It is shown that in all cases the characteristic temperature of the three-phase system corresponds with the vapour pressure of pure carbon dioxide, and thereby it follows that in each case solid carbon dioxide constitutes the solid phase. The equilibrium temperature lies only so much below the sublimation temperature as corresponds with the amount of the second component in the vapour phase. J. F. S.

The Phenomena Presented by Allotropic Organic Substances in Contact with a Solvent. H. VIXSEBOXSE (*Rec. trav. chim.*, 1921, **40**, 1—29).—In a study of the keto-enolic tautomerism of benzoylcamphor the author finds that the results obtained by Meyer's method (A., 1911, i, 350, 832) in alcohol, acetic acid, acetone, ether, or toluene as solvents do not agree satisfactorily with the formula of van't Hoff as elaborated by Dimroth (A., 1911, ii. 31; 1913, ii, 763), which the author considers to be a particular case of a general formula obtained by Smits (A., 1915, ii, 750). Using instead measurements of optical activity (compare Forster, T., 1901, **79**, 987) in alcohol, acetone, and toluene as solvents at three different temperatures, the author obtains results which agree well with Smits's formula. The equilibria in the different solvents are enol/ketone equals 82/18 in toluene, 61/39 in alcohol, and 52/48 in acetone. The author calculates that the transition temperature at which $c_A/c_B = l_A/l_B$, and therefore $K=1$, in other words, the temperature at which both forms can co-exist in the crystalline state, will be in the neighbourhood of $-83°$. W. G.

Non-mechanical Nature of Chemical Processes. M. POLANYI (*Zeitsch. Physik*, 1920, **1**, 337—344).—A mathematical paper, in which it is shown that so long as the deviations from the equi-partition principle cannot be explained without quanta, it appears to be objectless to represent chemical reactions in a mechanical manner. The dissociation of bromine takes place at least 300,000 times faster than is indicated by statistical mechanics.

J. F. S.

Origin of Chemical Energy. M. POLANYI (*Zeitsch. Physik*, 1920, **3**, 31—35. Compare preceding abstract).—It has been shown previously that chemical reactions do not occur at the expense of the kinetic energy of the reacting substances, but obtain the energy required for the reaction from the aether. The present paper shows that this energy is not drawn from the aether as heat radiation, and that such a source of energy is not possible or in keeping with dark reactions. The author considers the nature of the energy taken up in accordance with the hypothesis, and puts forward a further hypothesis as to the nature of the energy. The emission of radiation consists in a quantum spring made by an electron coupled with a quantum spring of the aether. The first spring is followed by a loss of energy which covers the energy used by the coupled quantum spring of the aether. The absorption of radiation consists in the reversal of this process. J. F. S.

Dynamic Quantum Weight, Nernst's Theorem, and Gibbs's Paradox. W. SCHOTTKY (*Physikal. Zeitsch.*, 1921, **22**, 1—11).—A theoretical paper, in which the influence of the dynamic quantum weight of solid substances and gaseous molecules on the chemical constant in vapour pressure and reaction equilibria is investigated for those cases where the weight differs from unity.

The weight unity is deduced for the lowest quantum condition from certain theoretical and experimental data, and this affords a confirmation of the Nernst theorem. The Nernst theorem cannot be extended to the higher quantum conditions of gaseous molecules, since here quantum weights which differ from unity certainly appear. A consideration of this case from the point of view of Gibbs's mixture paradox shows that this paradox has its foundation in the cellular structure of the phase volume. J. F. S.

Theory of Equations of Condition. I. MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **96**, 483—497).—In a previous paper (*Ann. Physik*, 1914, **45**) the author developed two equations of condition which have the form:

$$pv = RT\left[2 - e^{-n/RT\int_0^\infty F(r)dr} + b/v + a_1 b^2/v^2 + \ldots\right]$$

and $pv=$

$$RT_e{}^{-n/RT\int_0^\infty F(r)dr}\left[1 + \left(b/v \,.\, e^{-n/RT\int_0^\infty F(r)dr}\right) + a_1\left(b/v \,.\, e^{-n/RT\int_0^\infty F(r)dr}\right)^2 + \ldots\right]$$

In the paper quoted the value of $\int_0^\infty F(r)dr$ was not determined. The author now deduces the first of the above formula by the "Wall" method, and then proceeds to evaluate $\int_0^\infty F(r)dr$, which is shown to have the value:

$$n\int_0^\infty F(r)dr = RT \log_e RT/p(v-b) + RTv/(v-b) - RT + bp.$$

J. F. S.

The Significance of Velocity Constants from the Point of View of the Quantum Theory. MAX TRAUTZ (*Zeitsch. Physik*, 1920, **2**, 117—126, 296).—A mathematical investigation from the point of view of the quantum hypothesis of the two factors composing the velocity constant characteristic of a reaction—the frequency or impact number and the activity or yield factor. The work is concerned principally with the former, and includes a discussion from the point of view of the quantum hypothesis of the temperature-coefficient of the velocity of reaction. J. S. G. T.

Influence of Colloids on the Rate of Reactions Involving Gases. I. Decomposition of Hydroxylamine in the Presence of Colloidal Platinum. ALEXANDER FINDLAY and WILLIAM THOMAS (T., 1921, **119**, 170—176).

Kinetics of the Reaction between Hydrogen Peroxide and Iodine. E. ABEL (*Zeitsch. physikal. Chem.*, 1920, **96**, 1—179).—The reaction between hydrogen peroxide and iodine which is represented by the equation $H_2O_2 + I_2 = 2HI + O_2$ (1) is on account of the similarity of the reaction substances always accom-

panied by the reaction $H_2O_2 + 2HI = I_2 + 2H_2O$ (2), whereby a com plicated system is set up which is rendered more difficult of investigation because reaction (1) only takes place under otherwise suitable conditions between relatively narrow limits of hydrogen-ion concentration, namely, between $H^{\cdot} = 10^{-6}$—10^{-7}, with a velocity which is experimentally measurable. The velocity was ascertained by measuring the volume of oxygen evolved, and to prevent supersaturation large volumes of the reaction mixture were rapidly stirred. In order that the hydrogen-ion concentration should be maintained within the necessary limits, sodium acetate and acetic acid were added to the reaction mixture. The total changes occurring are represented by the scheme:

$$\overset{(a-x_1-x_2)}{H_2O_2} + \overset{(b-x_1+x_2)}{I_2} + \overset{(d-x_1+x_2)}{2CH_3{\cdot}CO_2Na} \longrightarrow O_2 + 2NaI + 2CH_3{\cdot}CO_2H \quad (1')$$

$$\overset{(a-x_1-x_2)}{H_2O_2} + \overset{(e+x_1-x_2)}{2CH_3{\cdot}CO_2H} + \overset{(c+x_1-x_2)}{2NaI} \longrightarrow I_2 + 2CH_3{\cdot}CO_2Na + 2H_2O \quad (2'),$$

where the bracketed quantities represent the momentary concentrations, x_1 and x_2 the progress of the reactions (1′) and (2′) at the time t. In most cases the reactions were carried out with $0{\cdot}4N$-sodium acetate. It is shown that the velocity of the reaction between hydrogen peroxide and iodine is strictly proportional to the concentration of the peroxide. It is also proportional to the concentration of the I_3' ions, but with concentrations of sodium acetate greater than $1{\cdot}0N$ the velocity is a little less than that required for strict proportionality. The reaction velocity is to a degree dependent on the products of the reaction in the sense that with increasing concentration of hydrogen ions and iodine ions it decreases. The hydrogen-ion concentration appears in the equilibrium equation raised to the power q, which has a value for the present experiment between -1 and -2, and which varies in the sense that with increasing I' concentration it increases, and in the concentrations of $I'=0$ to about $I'=0{\cdot}1N$ the value of q reaches a stationary value of $-1{\cdot}50$; with a further increase in the I' concentration the value of q decreases toward -2. In this region the variation of q between $-1{\cdot}0$ and $-1{\cdot}50$ with I' concentration can be well represented by the e function, $q = -1{\cdot}50 + 0{\cdot}50e^{-402{\cdot}5[I']}$. The iodine-ion concentration appears in the equation raised to a power which lies between -1 and -2. Apart from the above-mentioned connexion between the I' concentration and the velocity, the "order" of reactions (1) and (1′) in respect of the I' concentration may be so formulated that it passes through a minimum which lies at about -4 for very small concentrations of I' ions. On either side of this minimum the order increases, on the side of decreasing I' steeply toward -2 or perhaps to -1, and on the side of increasing I' concentration more slowly towards -1. This change in the index of the I' concentration, which represents the concentration range of $0{\cdot}001N$—$0{\cdot}1N$, may be represented by whole number stationary points ($-4{\cdot}0$, $-3{\cdot}0$, $-2{\cdot}0$, $-1{\cdot}0$), which represent practically sudden changes in

the character of the reaction and which subdivide the concentration range into four parts (I, II, III, IV), which may be easily fitted in with the four indexes. The approximate limits of these four parts, as well as the corresponding velocity-coefficients $\bar{k}_1$ for unit concentration of the reacting substances with 0·4N-sodium acetate at 25°, are given in a short table in the paper, and may be shortly reproduced, thus: region I, I′(0·001 – 0·004)N, $p = -4·0$, $\bar{k}' = 4·6 \times 10^{-17}$; II, I′(0·004 – 0·008)$N$, $p = -3·0$, $\bar{k}_1 = 13·3 \times 10^{-15}$; III, I′(0·009 – 0·02)$N$, $p = -2·0$, $\bar{k}' = 15·1 \times 10^{-13}$; and IV, I′(0·03 – 0·1)$N$, $p = -1·0$, $\bar{k}' = 5·8 \times 10^{-11}$. Under otherwise constant conditions the velocity increases with increasing acetate content; for a given I′ concentration this increase may be represented by the expression: $\bar{k}_{1[I']=0·3 \atop \lim[I_3']=0} = [2·67 + 12·0\alpha'(CH_3·CO_2Na) + 10·8(1 - \alpha')^2(CH_3·CO_2Na)^2] \times 10^{-11}$, where α' is the degree of dissociation and $(CH_3·CO_2Na)$ indicates the total concentration of sodium acetate in gram-mols. per litre. More generally, within the region I—IV the time law of reaction I′ is given by the simultaneous differential equations $dx_1/dt = \bar{k}_{1\,I:II:III:IV}\{(a - x_1 - x_2)[I_3']_t\}/[I']_t^{4:3:2:1}\{[K_E(e + x_1 - x_2)/a'd]^{1·50—0·50_e - 402·5[I']_t}\}$ and $dx_2/dt = \bar{k}_2(a - x_1 - x_2)[I']_t$, where the values for $\bar{k}_1$ are those given above, $\bar{k}_2$ is the equilibrium constant of the $H_2O_2 - I'$ reaction (0·78), and $[I']_t$ and $[I_3']_t$ represent the concentrations of I′ and I_3' ions, and are obtained from the tri-iodide equilibrium at time t for an iodide concentration $(c + x_1 - x_2)$ and iodine concentration $(b - x + x_2)$, and K_E is the dissociation constant of acetic acid ($1·8 \times 10^{-5}$). These equations have been tested on a series of examples and substantiated. The above relationships indicate that the $H_2O_2 - I_2$ reaction takes place with respect to H˙ and I′ negatively auto-catalytically, but in combination with the $H_2O_2 - I'$ reaction in relation to iodine positively; in respect of H˙ and I′, however, the nature depends on the conditions, that is, as $x_1 >$ or $< x_2$ negative or positive catalytic. The variations of the reaction $H_2O_2 - HI$ from the strictly bimolecular reaction which are found in the literature are all to be explained by the presence of the simultaneous reaction $H_2O_2 - I_2$.

J. F. S.

Removal of Halogens from some Organic Compounds. ARVID HJ. HEDELIUS (*Zeitsch. physikal. Chem.*, 1920, **96**, 343—366).—The velocity of reaction between solutions of sodium hydroxide and a series of halogen substitution products has been investigated at a series of temperatures. The measurements were all carried out in aqueous solutions, and from the results the constant A of the Arrhenius temperature formula,

$$K_{T_1} = K_{T_0} \cdot e^{(A[T_1 - T_0]/2T_0T_1)},$$

was calculated. The following data are recorded: monochloroacetic acid, 55°, $K = 2·05 \times 10^{-3}$; 65°, $K = 6·08 \times 10^{-3}$; 80°, $K = 23·9 \times 10^{-3}$; 90°, $K = 61·8 \times 10^{-3}$; $A = 23,000$; monobromoacetic acid, 65°, $K = 151 \times 10^{-3}$; 75°, $K = 365 \times 10^{-3}$; $A = 20,600$;

ethylene dibromide (first stage), 30°, $K = 113 \times 10^{-3}$; 45°, 649×10^{-3}; $A = 22{,}000$; (second stage), 75°, $K = 2{\cdot}8 \times 10^{-3}$; α-bromoacetoacetic ester, 40°, $K =$ ca. 800×10^{-3}. Experiments were also made with α-bromopropionic acid and monochloroacetone. In the case of α-bromopropionic acid, it was impossible to obtain a velocity constant, since the reaction takes place simultaneously in several directions. The influence of alcohol, water, and acetone on the velocity of the reaction has been examined. In the case of monochloroacetone, the constant was determined at 0°, as the reaction is extremely rapid, even at this temperature, and the constant shows a decided progression. J. F. S.

Kinetics of the Ketonic Decomposition of Acetoacetic Acid. ERIK M. P. WIDMARK (*Acta med. Scandinav.*, 1920, **53**, 393—421; from *Chem. Zentr.*, 1921, i, 9—10).—The course of the reaction is followed by estimation of the carbon dioxide evolved according to Winckler's method (precipitation of barium carbonate). The necessary acetoacetic acid is prepared by hydrolysis of technical ethyl acetoacetate by alkali hydroxide, this process being complete before acetone is produced in measurable amount. The formation of acetone has been investigated in acid and alkaline solution; in the latter, practically only the electrolytically dissociated anion of acetoacetic acid is present, since the salt is extensively dissociated into Na and $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2'$. In strongly acid solution, on the other hand, the acid is present as such, since electrolytic dissociation can be neglected. It is found that the undissociated and dissociated acids exhibit greatly differing rates of decomposition, that of the former being about fifty times the greater. In alkaline solution, formation of acetone occurs at the rate of decomposition of the anion, the velocity of which is calculated from a series of concordant observations to be 0·00008 at 37°; in strong mineral acid solution, on the other hand, it occurs at the rate of decomposition of the acid itself, the constant of which is calculated to be 0·0042 at 37°. As is to be expected, the reaction is of the first order in either case. In almost neutral solutions, in which the acetoacetic acid is partly dissociated, the rate of decomposition depends on the degree of electrolytic dissociation, and can be calculated from the expression $\alpha V_1 - (1 - \alpha) V_m$ (V_1 and V_m = constants of decomposition of the ion and undissociated acid respectively; α = degree of dissociation). This expression is valid for all concentrations of hydrogen ions. On the other hand, the degree of dissociation depends on the hydrogen-ion concentration, which varies with the progress of the action, since acetoacetic acid is decomposed. In spite of these complications, the author has succeeded in establishing the validity of his hypothesis; in nearly neutral solution, the velocity constants gradually diminish, in consequence of falling hydrogen-ion concentration, and the extent to which this occurs harmonises well with the theoretical calculations. On the other hand, the hydrogen-ion concentration can be maintained constant by the addition of acetic acid and sodium acetate, and in this case the

velocity constants become uniform. Under these conditions, the hydrogen-ion concentration can be estimated by a study of the rate of reaction, and the value thus found is identical with that determined by electromotive measurements. H. W.

Kinetics of the Reduction of Azo-compounds. HEINRICH GOLDSCHMIDT and ASBJÖRN BRAANAAS (*Zeitsch. physikal. Chem.*, 1920, **96**, 180—213).—The velocity of the reduction of acid solutions of a number of azo-compounds by means of stannous chloride or stannous bromide has been followed at 25° by means of colour changes, which were observed with a Dubosq colorimeter. The reduction of azobenzenetrimethylammonium chloride, azobenzene-*mm'*-disulphonic acid, *p*-dimethylaminoazobenzene, *p*-diethylaminoazobenzene, *p*-aminoazobenzene, methyl-orange, β-naphthylaminoazobenzenesulphonic acid, benzeneazonaphthylamine-4 : 7-disulphonic acid, naphthionic-azobenzenesulphonic acid, *p*-tolueneazo-*p*-toluidine, methylene-blue, chrysoidine-T, *p*-oxyazobenzene, tropæolin-T, α-naphtholazobenzenesulphonic acid, β-naphtholazobenzenesulphonic acid, benzeneazo-β-naphtholsulphonic acid-S, benzeneazo-β-naphtholdisulphonic acid-R, and *m*-xyleneazo-β-naphtholdisulphonic acid-R in hydrochloric acid (0·1—1·0*N*) in the absence of, and in the presence of, various concentrations of sodium chloride by solutions of stannous chloride of various concentrations has been investigated. In the case of six of the above-named compounds, the reduction has been effected with stannous bromide in hydrobromic acid solution. In every case, the reduction is found to be a bimolecular reaction, since the velocity of reduction is proportional to the tin concentration. In those cases where the azo-compound is broken up into two amino-derivatives by the addition of four hydrogen atoms, the reaction takes place in two stages. The first stage, which occurs with a measurable velocity, consists in the reduction to a hydrazo-compound, which is then further reduced with an infinitely large velocity. In most cases, the reduction takes place, as in the case of nitro-compounds, by means of the small amount of $SnCl_3'$ which always exists in acid solutions of stannous salts, but, in addition, the stannous salt can exercise a reducing action. Both actions may occur simultaneously. As examples of the reduction by the $SnCl_3$ ion, the cases of β-naphthol-orange and aminoazotoluene may be quoted, whilst benzeneazo-β-naphtholsulphonic acid-S, benzeneazo-β-naphtholdisulphonic acid-R, and *m*-xyleneazo-β-naphtholdisulphonic acid-R furnish examples of the combined action. In the first case, the velocity constant is given by $k = K[Hlg']$, and is proportional to the halogen-ion concentration. In the second case, the formula is $k = K_1 + K_2[Hlg']$. The halogen acid can be replaced by the metallic haloids without change of the velocity of reaction; this is in keeping with the above formulæ. In many cases it is not the azo-compound itself, but a small concentration of the additive compound of the azo-compound with the halogen acid, which undergoes the primary reduction. When this additive compound reacts with the $SnCl_3$ ion, the reaction velocity is given by the formula

$k=K[H^{\cdot}][Hlg]^2$, which, in the absence of metallic haloid, becomes $k=K[Hlg\mathrm{H}]^3$. These formulæ were obtained for the substances azobenzenetrimethylammonium chloride, azobenzene-*mm'*-disulphonic acid, and the four *p*-aminoazo-compounds. In these cases, an addition of metallic haloid increases the velocity, but not to the same extent as the addition of an equivalent quantity of hydrogen haloid would do. Cases were observed where the reaction follows the equation $k=K_1[Cl'] + k_2[H^{\cdot}][Cl]^2$, in particular that of oxyazobenzene. In this case, the reaction takes place between the azo-compound itself and its additive compound with $\mathrm{Sn}Hlg_3'$. The investigation of α-naphthol-orange indicates that the tin haloid reacts with the acid additive compound. If this were the only reaction, the course would be represented by $k=K[H^{\cdot}][Cl']$, but $\mathrm{Sn}Hlg_3'$ also appears to react, so that the equation must be changed to $k=K_1[H^{\cdot}][Hlg'] + K_2[H^{\cdot}][Hlg]^2$. Stannous bromide reduces more rapidly than stannous chloride, but not regularly; the relationship between the two reducing actions varies very much in different cases, but in all cases the course of the reactions are identical. The catalytic action of the halogen and hydrogen ions is not dependent to any extent on the degree of dissociation, but appears to be proportional to the total concentration of the strong electrolyte. J. F. S.

The Catalytic Decomposition of Hydrogen Peroxide by Sodium Iodide in Mixed Solvents. VAN L. BOHNSON (*J Physical Chem.*, 1920, **24**, 677—700).—A study of the velocity of catalytic decomposition of hydrogen peroxide by sodium iodide, as influenced by the medium in which it takes place. The solvents used were different aqueous mixtures of methyl, ethyl, *n*-propyl, *iso*butyl and amyl alcohols, glycerol, and pyridine. The solvents apparently did not undergo oxidation, and the decomposition of the hydrogen peroxide, which was measured gasometrically, was complete. The relative velocity of reaction in the pure solvents may be expressed by the following constants: methyl alcohol 23, ethyl alcohol 45, *n*-propyl alcohol 164, *iso*butyl alcohol 397, amyl alcohol 537, glycerol 376, pyridine 7, water 128·7, and for a gelatin solution with marked viscosity 94·3. There is apparently no relation between the velocity of the reaction and the dielectric constant, viscosity, or surface tension of the pure solvent. In some cases, the curves for the reaction velocity in aqueous mixtures showed minima, which, however, did not correspond with the minima in the fluidity curves.

The solvent appears to exert a specific influence on the velocity of a reaction, this effect being probably the resultant of a number of other effects, due to association of the solvent, its viscosity, and surface tension, the dissociation of the catalyst, and a possible reaction between solvent and dissolved substances. W. G.

Hydrogenation of Aromatic Compounds by the Help of Platinum. IV. The Dependence of Catalytic Hydrogenation on the Presence of Oxygen. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 1921, **54**, [*B*], 113—138. Compare Willstätter and Jaquet, A., 1918, i, 391).—In a previous

communication (*loc. cit.*), the authors have been led to the conclusion that platinum itself, and platinum loaded with oxygen, are to be regarded as distinct catalysts, but by the former term the metal is understood as not having been specially treated with oxygen. It is now shown, however, that platinum and palladium, whether as spongy metal or as colloid, are incapable of bringing about the hydrogenation of even the most reactive olefines if they have been freed completely from oxygen. Hydrogenations, dehydrogenations, and hydrogen peroxide catalyses by the platinum metals therefore depend alike on the presence of compounds of the metal and oxygen. Sabatier's conception of catalytic hydrogenation by finely divided metals as due to the formation of an unstable hydride must therefore be abandoned, since the intermediate compounds contain both hydrogen and oxygen (compare, also, Hofmann and Ebert, A., 1917, ii, 25; Hofmann and Zipfel, A., 1920, ii, 240). Confirmation of this view is found in the observations of Mond, Ramsay, and Shields, who, however, do not express any definite opinion as to the manner in which the gases are present. Generally, however, it appears to have been assumed that hydrogen, and probably oxygen, are present in the monatomic form, but the authors' experiments indicate that the former is present in oxidised platinum and palladium in a more readily dissociable form than in the hydrides of these metals. It appears more probable that the oxidised metal reacts with hydrogen in such a manner as to yield a compound, which is both a peroxide (or oxide) and hydride, and that the transference of hydrogen depends on the metal functioning alternately as a bi- and quadri-valent element: (i) $Pt + O_2 \rightleftharpoons Pt{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ $Pt{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix} + H_2O = Pt{<}\begin{smallmatrix}O\cdot OH\\OH\end{smallmatrix}$; (ii) $Pt{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ (or hydrate) $+ H_2 \rightleftharpoons \begin{smallmatrix}H\\H\end{smallmatrix}{>}Pt{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ (or hydrate).

It is pointed out that the hydrogenation of aromatic carboxylic acids by means of sodium amalgam takes place in a manner which differs from that of all other methods of reduction, since the partly reduced, and therefore olefinic, acids are less readily attacked than the parent substances. The phenomenon resembles that of paralysis of the catalyst, and is being investigated further.

The preparation of spongy platinum by the reduction of chloroplatinic acid by formaldehyde in alkaline solution (Willstätter and Hatt, A., 1912, i, 545) is improved by the substitution of potassium for sodium hydroxide, since the slower reduction, due to the formation of the sparingly soluble potassium platinichloride, allows the temperature to be more readily controlled. The catalyst may be freed completely from oxygen by treating its suspension in glacial acetic acid with hydrogen for thirty hours at the atmospheric temperature, or eight hours at 50—60°. It is then completely insoluble in hydrochloric acid, and does not liberate iodine from acidified potassium iodide solution. It is incapable of causing the hydrogenation of benzene, *cyclo*hexene, limonene, or pyrrole, but acquires this power if shaken for a short period with

air. Deoxidation of the catalyst also invariably takes place during the course of hydrogenation with greater or less rapidity, according to the particular substance under investigation, and the "poisoning" action of certain substances, such as glycerol and thiophen, is certainly due to the same cause, but it is doubtful if all cases of paralysis of the catalyst can be explained by the removal of oxygen. Removal of oxygen by diminution of pressure can only be accomplished with difficulty, but, by continuous exhaustion with a high vacuum pump, it was found possible to get a nearly inactive preparation.

Hydrogenation of a di-olefine could not be effected in the presence of palladium-black which had been freed completely from oxygen, whilst oxygen-free colloidal palladium was also found to be inactive.

Catalytic hydrogenation in the presence of nickel preparations has been regarded by Sabatier ("La Catalyse," 1913, p. 115) as exclusively a property of the metal; the function of the oxides of nickel has, however, been recognised by Bedford and Erdmann (A., 1913, i, 701), whilst Brochet (A., 1914, i, 645) has expressed the opinion that pure nickel is catalytically inactive. The authors' experiments show that whilst nickelous oxide and nickel suboxide are active, the metal itself, even when prepared at the lowest possible temperature, is inactive in the presence of sodium cinnamate, oleic acid, or methyl oleate, but acquires activity when primed with oxygen, the quantity of the latter which is required being very small.

The explanation of the rôle of oxygen in catalytic hydrogenations in the presence of platinum enables the technique of the operation to be improved considerably, since the catalyst is reactivated by oxygen as soon as it shows signs of diminished activity, and "poisoning" is circumvented either by increasing the amount of platinum or by suitable treatment with oxygen. Priming is particularly useful when only small quantities of catalyst are used or when it is employed frequently. According to the authors' experiments, the use of spongy palladium has no advantage over that of platinum (contrast Wieland, A., 1912, i, 956), whilst, on the other hand, the greater absorption capacity of the former for hydrogen renders more difficult its reactivation by oxygen to such an extent that the procedure becomes either dangerous or cumbersome.

According to Böeseken and his co-workers (A., 1916, ii, 239; 1918, ii, 73), the process of catalytic reduction by finely divided metals depends on a diffusion phenomenon which precedes the actual hydrogenation and controls the rate of reaction, since it is assumed to take place more slowly than the actual reduction. This hypothesis does not explain the very different rates of hydrogenation of benzene and *cyclo*hexene under similar conditions, since it is improbable that the diffusion process can differ greatly in the two cases, or the cessation or delay after addition of a molecule of hydrogen to cinnamic acid. It appears more probable that the rates observed in catalytic hydrogenations depend on two

factors: (i) the actual velocity of hydrogenation, and (ii) the decrease in the amount of catalyst, since the spongy or colloidal metal, which contains oxygen, is reduced to the inactive metallic hydride, whilst it transfers hydrogen to the substance under investigation. Since the loss of oxygen from the catalyst frequently seems to take place with uniform rapidity, it is possible to compare the activities of unsaturated substances by comparison of the volumes of hydrogen which are transferred to them by a given weight of oxygenated platinum before the latter becomes exhausted. Alternatively, the initial rates of hydrogenation may be compared. The results obtained by the two methods are similar.

Substances may be divided into three groups, according to their rate of hydrogenation: (i) ethylenic compounds, with which the process occurs so readily that deoxygenation is scarcely noticeable, and need not be taken into account if the catalyst is only used once; (ii) simple aromatic substances, which are moderately rapidly hydrogenated (but much more slowly than the olefines), and with which removal of oxygen may cause a great decrease in the activity of small amounts of catalyst; and (iii) difficultly hydrogenated substances, which can only be reduced after activation by the method of Willstätter and Jaquet (*loc. cit.*); the rate of hydrogenation is so small that deoxygenation of the platinum occurs with inconvenient rapidity. Polynuclear aromatic compounds, such as *o*-benzylbenzoic acid, *o*-naphthoylbenzoic acid, and substances which directly remove oxygen from the platinum, belong to this class.

The peculiar suitability of glacial acetic acid as a solvent in catalytic hydrogenations is not due to a greater solubility of hydrogen in this substance than in the other media frequently employed. H. W.

A New Periodic Relationship between the Atomic Weights of the Chemical Elements. V. Calculation of Rydberg's Constant. KARL FEHRLE (*Physikal. Zeitsch.*, 1921, **22**, 60—62. Compare A., 1920, ii, 303, 540, 749).—A theoretical paper, in which it is shown that series spectra are due to tensions, which are due to the incomplete resonance between the vibrations of the atoms of a molecule and those of complexes of a number of n^4 molecules, when n indicates any whole number. The energy of the tension is equal to one-half of the difference of the energy of rotation of the molecule, which is produced when these change their angular velocity by an amount which would be necessary to produce resonance with the complexes under consideration, and the energy of the emitted radiation equal to the change of energy accompanying changes in the complex. The relationship of the angular velocities is the same as when all the atoms are arranged on the surface of a single sphere. On the basis of the above, the atom model and the unchanged constants of the radiation formula of the previous work, it is shown that the portion of the formula which is variable for a given element is identical with Bohr's formula. The constants,

although they contain completely different quantities and are derived from a different point of view, are identical with Rydberg's constants to the second place of decimals. J. F. S.

Bohr's Atomic Model and the Theory of Relativity. K. FÖRSTERLING (*Zeitsch. Physik*, 1920, **3**, 404—407).—A theoretical paper, in which it is shown from the Bohr frequency conditions and perfectly general assumptions that just those displacements of the spectrum lines occur which are demanded by the theory of relativity. J. F. S.

Spatial Atomic Models. ADOLF SMEKAL (*Zeitsch. Physik*, 1920, **1**, 309—319).—A theoretical paper, in which the existence of an electron ring or an electron sheath in the atom is discussed. J. F. S.

Dynamics of Spatial Atomic Structure. A. LANDÉ (*Zeitsch. Physik*, 1920, **2**, 83—86).—The author applies the analysis developed in a previous paper (A., 1920, ii, 540) in connexion with the motion of four electrons arranged tetrahedrally about a nuclear charge to the cases of (*a*) eight electrons spatially distributed in cubical formation about a large nuclear charge, (*b*) six electrons rhombohedrally distributed about the nucleus, and (*c*) three electrons similarly arranged with regard to the nucleus. The characteristics of the various orbits, their inclinations to one another, etc., are discussed. The orbits of the spatially distributed electrons are analogous to the Keplerian orbits deduced by Sommerfeld by the application of the principle of relativity. A spatial distribution of four electrons, the effect of neighbouring electrons being neglected, is less stable than a plane ring formation of four electrons, whereas the opposite is the case where six electrons are concerned. J. S. G. T.

Size of Atoms. A. LANDÉ (*Zeitsch. Physik*, 1920, **2**, 87—89).—Values for the radii of the alkali and halogen ions deduced from the cubical structure of alkali-halogen salts are not in agreement with the more certain values deduced from the consideration of the *X*-ray and ordinary spectra series of lines of these elements. This discrepancy may be removed by assuming that in neutral alkali atoms the ions enclosed within the valency electrons and arranged so as to produce cubical symmetry move in circular orbits, while a large association of elliptic orbits possessing cubical symmetry occurs. A similar assumption may be made in the case of the atoms of the inert gases and negative halogen ions. J. S. G. T.

Cubical Atoms, the Periodic System and Molecular Structure. A. LANDÉ (*Zeitsch. Physik*, 1920, **2**, 380—404).—The orbits of four and eight electrons arranged so as to afford cubical symmetry are discussed. Any number of electrons may be

arranged so as to afford a lower order of symmetry, and the characteristics of the respective orbits about a nuclear charge are discussed. The orbits of individual electrons are approximately circles or Keplerian ellipses. The orbits affording cubical symmetry, in the case of eight electrons, have been shown by Madelung and Landé to afford a more stable configuration than a plane ring of eight electrons. In the case of the ionised alkalis, the cubical formation is considerably more stable than any other configuration. The neutral sodium atom would be represented by nine electrons rotating about a nuclear charge equal to $9e$. The nine electrons would be arranged in a formation of eight inner electrons in cubical formation and an outer orbit described by the remaining electron. Such a disposition would be characterised by possessing less energy than another possible stable arrangement of five inner and four outer electrons. From the consideration of such a formation, the value of the radius of the sodium ion is found to be 0.605×10^{-8} cm., in agreement with value 0.517×10^{-8} cm. found by Fajans and Herzfeld from crystal lattice results. In like manner the respective radii of the neon, fluorine, and oxygen ions are found to be 0.714×10^{-8} cm., 0.875×10^{-8} cm., and 2.2×10^{-8} cm. The radius of the neutral carbon atom is 1.30×10^{-8} cm. The ionisation potential for neon is calculated as 23·8 volts, a value in agreement with anticipations based on the values 15·1 volts and 17 volts determined by Holst and Hoopmanns, and Horton and Davies respectively for argon. The electronic affinity for the fluorine atom is calculated, and is found to be 132 Cal. per mol., in agreement with the series of values 119, 84, and 77 Cal. per mol. found by Born (A., 1920, ii, 156) for the respective electronic affinities of chlorine, bromine, and iodine. The heat of ionisation of HF is calculated and found to be 350 Cal. per mol. This value is in agreement with the respective values 320, 311, and 302 Cals. per mol. deduced by Born (*loc. cit.*) from thermochemical and physical data in the cases of hydrogen chloride, bromide, and iodide. The nuclear distance for hydrogen fluoride is calculated and found to be 0.945×10^{-8} cm., in agreement with the value 0.92×10^{-8} cm. deduced by Krazer. The heat of ionisation of water is found to be 533 Cals. per mol. and the nuclear distance 2.03×10^{-8} cm. J. S. G. T.

A Dynamical Model of a Cubical Atom. E. MADELUNG and A. LANDÉ (*Zeitsch. Physik*, 1920, **2**, 230—235).—An atomic model composed of eight electrons arranged in the manner previously described (preceding abstract) so as to afford cubical symmetry is characterised by the fact that the intrinsic potential energy of such an atom is greater than that of a plane ring of eight electrons, and, moreover, the orbital perturbations produced by the action of an impressed force are of a much higher order of magnitude than that of the latter. These defects are absent from an atomic model constituted of two interpenetrating tetrahedral models, and the dynamics of such an atomic model are investigated mathematically.

J. S. G. T.

The Constitution of Atoms. ORME MASSON (*Phil. Mag.*, 1921, [vi], **41**, 281—285).—The word *baron* (Greek, *βαρος*, weight) is suggested for the positively charged particles contained in the atoms. Rutherford, in a footnote, remarks that the word *proton* has met with considerable approval as the name for this elementary atomic constituent. The symbol *b* denoting one boron, and *e* one electronic charge, the formula $(b_2e)_N(be)_n$, where N is the appropriate atomic number, and n has any appropriate value from 0 to 54, represents the constitution of the respective nuclei of all the elements from He to U. In the case of the elements He, C, N, O, S, the lower isotopes of B, Ne, Si, and Ar, and probably the lower isotopes of Li, Mg, Ca, and some other light elements, $n=0$. For hydrogen, $n=-1$. A neutral atom has the formula $[(b_2e)_N(be)_n]e_N$. The notation is applied to the sub-atomic reactions accompanying the emission of an α-particle, the emission of a β-ray, and the bombardment of light atoms by swift α-particles [*p* should be substituted for *b* in the above formulæ if the name *proton* is adopted]. J. S. G. T.

The Hydrogen Atom, Atomic Ether, and Planck's Quantum. L. ZEHNDER (*Vierteljahrschr., naturf. Ges. Zürich*, 1920, **65**, 59—92; from *Chem. Zentr.*, 1921, i, 236).—According to the author, the atomic aether surrounds the earth as an aether shell and thus explains the negative result of the Michelson-Morley experiment. In a similar manner aether masses are supposed to surround the atoms as condensed layers. The presumably spherical hydrogen atom enclosed in a shell of this type may exhibit two types of elastic oscillation when it collides with a second hydrogen atom, and these together correspond with optical observations. The mass of the individual atom of aether is calculated to be about 1/20,000th part of that of an electron. The oscillation in the atomic nucleus and aether shell, on the one hand, and the vibrations on the other are illustrated by Riecke's double pendulum. The oscillations may either be regarded as elastic or electric. Bohr's electric interpretation can be improved if account is taken of the vibrations. According to Hamilton's principle, Planck's quantum is connected with the addition of an aether atom to the aether shell. H. W.

The Sizes of the Kations of the Alkali Metals. RICHARD LORENZ (*Zeitsch. Physik*, 1920, **2**, 175—180).—The respective diameters of the ions of the alkali metals lithium, sodium, potassium, rubidium, and cæsium derived from the work of various authors (Born, Landé, Born and Lorenz, Heydweiller) are tabulated. Such tabulated values include the following: R_A, the radius deduced from the atomic volume; R_W, the value deduced from the value of the heat of hydration; R_B, the radius deduced from considerations of ionic mobility employing the Stokes-Born formula; R_G, the value deduced from the space-lattice constant; R_R, the value deduced from considerations of ionic refraction; R_D, the radius deduced from diffusion of the alkali metals in mercury, employing the Stokes-Einstein formula; $R_{\psi(0\cdot25)}$, the value obtained on the assumption

that the ions occupy the smallest possible fraction, 0·25, of the total volume of the atom; and R'_W the values deduced from the corresponding values, R_W, by deducting therefrom the radius 0.45×10^{-8} cm., a correction pointed out by Born. The values of R_R and R_G are in good agreement. The values of R_W and R_B are respectively greater and less than the corresponding values of R_G or R_R. The values $R_{\psi(0.25)}$ and R'_W are in very close agreement, and probably represent very approximately the radii of the respective ions of the alkali metals. For lithium, sodium, potassium, rubidium, cæsium, the respective values of $R_{\psi(0.25)}$ in 10^{-8} cm. are 1·09, 1·33, 1·66, 1·78, 1·92. The respective values of R'_W are 1·04, 1·14, 1·55, 1·79, and 1·77. J. S. G. T.

Proximity of Atoms in Gaseous Molecules. A. O. RANKINE (*Proc. Roy. Soc.*, 1921, [*A*], **98**, 360—369).—There is substantial agreement between the atomic dimensions deduced from *X*-ray crystal measurement and from the viscosity by the kinetic theory. In size and shape the atoms of the monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table. The Lewis-Langmuir theory accounts satisfactorily for the viscosity relations of oxygen, chlorine, bromine, and iodine in relation to the behaviour of the corresponding inert atoms neon, argon, krypton, and xenon. A chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, that is, with the outer electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms and iodine to xenon. An oxygen molecule has the same size and shape as two neon atoms with their outer electron shells coincident.

The best model of the hard elastic body to which a molecule composed of two equal atoms is equivalent is a spheroid. The volume of this spheroid is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is separately equivalent. The nitrogen molecule appears to be equivalent to a hard, elastic body nearly spherical in shape. The atomic diameters recalculated from viscosity measurements are: neon, 2·35; argon, 2·87; krypton, 3·19; xenon, 3·51; nitrogen, 3·13, all in cm. $\times 10^{-8}$. The effective mean areas are calculated as: oxygen, 0·69; chlorine, 1·07; bromine, 1·28; iodine, 1·56, all in cm.$^2 \times 10^{-15}$. J. R. P.

The Similarity between Carbon Dioxide and Nitrous Oxide. A. O. RANKINE (*Proc. Roy. Soc.*, 1921, [*A*], **98**, 369—374).—The molecules of carbon dioxide and nitrous oxide behave not merely as though they had the same size and shape, but also as if each had an external electron arrangement practically the same as that of three neon atoms in line and contiguous. A hypothetical molecule composed of three neon atoms with their centres in line and 1.30×10^{-8} cm. apart would correspond, on the kinetic theory of viscosity, with a mean target area of 0.895×10^{-15} cm.^{2} The viscosity data lead to the values 0.870×10^{-15} cm.^{2} for carbon

dioxide and $0{\cdot}867 \times 10^{-15}$ cm.^{2} for nitrous oxide. Within the limits of experimental error the molecules of the two gases behave in the gaseous state as though they were of identical size and shape. This result is in agreement with Langmuir's theory (A., 1919, ii, 328).

J. R. P.

Structure of Some Compounds. GERHARD KIRSCH (*Zeitsch. physikal. Chem.*, 1920, **96**, 471—473).—On the basis of Kossel's hypothesis (A., 1916, ii, 243), that the stability of the nitrogen molecule is due to an additional nucleus, and that the similarity of the CN group to the halogens is due to this cause, the author considers other molecules, such as carbon monoxide, ozone, nitrogen dioxide, nitrous oxide, and the –CNO radicle. He considers that similar stabilising nucleii are present in these, and explains the endothermic character of these substances on this basis. J. F. S.

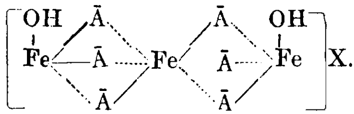
The Geometry of the Co-ordination Number. GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1920, **114**, 24—26).—As a contribution to the problem of isomerism in co-ordinated compounds, the author has calculated the limiting radius of each of n spheres surrounding and in contact with a central sphere of unit radius, for the cases where n is 3, 4, 5, 6, 8, 12, or 20. When $n=5$ the limiting radius is the same as when $n=6$, namely, 2·414, but the disposition of the spheres in the former case is indeterminate. When n is 8, there are two possibilities; if the spheres are situated at the corners of a cube, $r=1{\cdot}366$, but if at the corners of an archimedian antiprism, $r=1{\cdot}549$. For higher values of n the number of possible solutions of the problem becomes greater, and a new kind of isomerism becomes a possibility in such cases. E. H. R.

The Space Significance of the Co-ordination Number in Polynuclear Compounds. HANS REIHLEN (*Zeitsch. anorg. Chem.*, 1920, **114**, 65—89).—A theoretical paper, in which the spatial arrangements in co-ordinated compounds containing several nuclei are discussed, and also the relationship between the co-ordination number and the possible spatial arrangements. In tri-nuclear compounds, if each nucleus preserves the octahedral form, the minimum co-ordination number is 12. In such compounds it must be supposed that two outer octahedra are each combined with the middle octahedron in such a way that the last shares one of a pair of parallel faces with each outer octahedron. Six groups then form "bridge linkings" between octahedra, as in the compound:

$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]X_4.$$

Many tri-nuclear compounds are known, however, with the co-ordination number 8, prominent among these being the red ferri-salts of organic acids of the general formula $[Fe_3\bar{A}_6(OH)_2]X$, where $\bar{A}$ is a fatty acid group. In such cases the author proposes to repre-

sent the middle nucleus of the chain by an octahedron and each of the two end nuclei by a tetrahedron, the combined geometrical form being an elongated rhombohedron. In other words, the central nucleus has a co-ordination number 6 and each of the end nuclei 4, as represented by the formula:



The mixed chromi-ferri-compounds, such as

$$[CrFe_2(OAc)_6(OH)_2]Cl,6H_2O,$$

are of interest because they should show isomerism, in which the difference is caused by the substitution of iron for chromium in the central nucleus. Such isomerism has not been observed, however, probably because chromium has much less tendency than iron to form nuclei of the tetrahedral type. The author's theory is also supported by the properties and composition of the complex ferribenzoates. Many of the compounds prepared by Weinland and his collaborators are discussed from the author's point of view, and in some cases modified formulæ are suggested.

Compounds with the co-ordination number 10, for example, $[Cr_3(OAc)_6SCN,H_2O(OH)_2]$, can be represented spatially by means of a chain of two octahedra and a tetrahedron. A number of trichromiacetate compounds appear to have the co-ordination number 11, for example, the pyridine compound

$$[Cr_3(OAc)_6(C_5H_5N)_3(OH)_2]I.$$

The constitution of these substances can be explained geometrically by supposing three octahedra to be joined so as to have one edge common to all three. Between the two outer octahedra there is then an acute angle of about 33°, and by a slight distortion the faces of the two octahedra thus separated can be brought into contact so that the three octahedra form a solid figure having eleven points. Geometrically, these eleven points fall into three groups of six, three, and two points respectively, corresponding with the chemical character of the compounds of this class.

Complex co-ordinated compounds containing four nuclei are discussed from a similar point of view, and geometrical structures of the same type are suggested for them. The nature of the "bridge linking" combining the several nuclei in the molecule is also discussed. E. H. R.

Use of Gold–Palladium Alloy for Crucibles. H. S. Washington (*J. Washington Acad. Sci.*, 1921, **11**, 9—13).—For fusions of silicates with sodium carbonate, crucibles of palau, an alloy consisting of gold 80% and palladium 20%, have been employed. Apart from its lower cost as compared with platinum and iridium–platinum, this alloy has the advantage that, after fusions, the fused mass may be easily and completely removed by treatment with hot water, the superior hardness and high polish

of palau facilitating this. As regards durability, it was found that the average loss with palau crucibles, after forty-seven fusions, was 0·2 mg., whilst with iridium–platinum, after twenty-one fusions, the amount was 0·4 mg.; in the latter case, volatilisation of iridium would account for part of the loss. No comparative figures for platinum were obtained. W. J. W.

Apparatus for Simultaneous Pressure and Volume Measurements of Gases. GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1920, **114**, 161—173).—An apparatus is described in which the pressure and volume of a gas liberated in any reaction may be determined at any moment. Gas may be added to or withdrawn from the system at any time, and the composition of the residue determined. The apparatus consists essentially of a detachable tube for the solid, connected through a detachable stopcock with a bulb communicating with a manometer. The volume of each part of the apparatus is known. The whole apparatus is exhausted, and gas admitted to the bulb and upper part of the stopcock. The manometer is read, and the initial volume of gas calculated. The stopcock is then opened, and from the manometer readings the pressure and volume of the gas are readily calculated. By means of the apparatus, the existence of $FeCl_3,12NH_3$ (9 mm. at $-79°$); of $AgBr,3NH_3$, and of $Ca,6NH_3$ could be demonstrated. In the last case, a secondary reaction, $Ca,6NH_3 = Ca(NH_2)_2 + 4NH_3 + H_2$ occurs, as well as a slow absorption of hydrogen in the solid phase. J. R. P.

Martin Heinrich Klaproth. RICHARD MEYER (*Zeitsch. angew. Chem.*, 1921, **34**, 1—3).—A biography of this German chemist, born 1743, died 1817. Klaproth's work dealt mainly with inorganic and mineralogical chemistry; he investigated the composition of sulphur trioxide, zirconite, cerite, and other rarer minerals, and detected the presence of nickel in meteorites. W. P. S.

Inorganic Chemistry.

Chloroform Solutions of Hydrogen Chloride. E. J. Williams (*Chem. News*, 1921, **122**, 62).—Hydrogen chloride can be absorbed by chloroform to a concentration of about 10 grams per litre. The equilibrium between solvent and solute is unstable, and unless the solution is kept in a closed vessel the gas passes completely out of solution. J. R. P.

Solubility of Sulphur in Alkali Hydroxides in the Cold. G. Calcagni (*Gazzetta*, 1920, **50**, ii, 331—340).—The author has

investigated the action on sulphur in the cold of the following solutions: 66% sodium (or potassium) hydroxide solution, ammonia solution (D 0·888), and solutions, saturated in the cold, of calcium, barium, and magnesium hydroxides, the last containing the solid oxide; as the sulphur dissolved, a fresh quantity was added until a condition of equilibrium was reached. The action of light produced no sensible effect on the velocity of dissolution of the sulphur. Analysis of the final solutions obtained gave the following results.

Sodium hydroxide: 100 c.c. contained 24·55 grams of sulphur, 57 parts of the latter being dissolved per 23 parts of sodium present. Potassium hydroxide: 100 c.c. contained 17·70 grams of sulphur, 59·35 parts of the latter being dissolved per 39·15 parts of potassium. Ammonia: 100 c.c. contained 1·367 grams of sulphur. Calcium hydroxide: 100 c.c. contained 0·1116 gram of sulphur; 32·3 parts of sulphur are dissolved per 40 parts of calcium, this amount corresponding with the formation of calcium sulphide. Barium hydroxide: 100 c.c. dissolves 2·60 grams of sulphur. When the sulphur attains a certain concentration, acicular crystals of barium tetrasulphide, BaS_4, are deposited. Magnesium hydroxide: 100 c.c. dissolves 0·014 gram of sulphur, the relation between the magnesium and sulphur present in the solution being 24·38 : 63·38, which corresponds with MgS_2.

All the solutions respond to the reaction for sulphides, polysulphides, thiosulphates, and sulphites. The conclusion is drawn that the reactions between sulphur and alkali hydroxides are highly complicated and gradual, the dissolved sulphur first forming sulphides, from which thiosulphates and, by further dissolution of sulphur, polysulphides are formed; the thiosulphates, losing part of their sulphur, yield sulphites. In the solutions more concentrated in sulphur, part of the latter appears to exist merely dissolved and uncombined, since these solutions yield sulphur to hot benzene.

All the solutions are decomposed by carbon dioxide, with separation of sulphur and liberation of hydrogen sulphide. Thus carbon dioxide acts similarly to mineral acids, but more slowly.

T. H. P.

Preparation of Sulphur Dioxide. VEREIN CHEMISCHER FABRIKEN MANNHEIM (Brit. Pat. 149662; from *Chem. Zentr.*, 1921, ii, 19).—Gaseous sulphur dioxide is obtained by heating the sulphates of the alkaline earth metals, magnesium, or iron in the presence of iron or other suitable metals or their lower oxides, or of carbon, at a comparatively low temperature. The reduction is first effected at 600°, whilst the evolution of sulphur di- and trioxides takes place at 900° in a current of steam and air.

H. W.

Preparation of Sulphuric Acid. T. SCHMIEDEL and H. KLENCKE (Brit. Pat. 149648; from *Chem. Zentr.*, 1921, ii, 19).—Gases containing sulphur dioxide are brought into intimate contact with as large a quantity as possible of nitrosylsulphuric acid

(54—58° Bé.); any gas remaining unabsorbed, and the nitrous vapours evolved from the sulphuric acid, are treated with acid of the same concentration as that in the mixing vessel. H. W.

Point Discharge in Nitrogen. M. PIRANI [with E. LAX] (*Wiss. Veröffentl. Siemens-Konzern*, 1920, **1**, 167—178; from *Chem. Zentr.*, 1921, i, 200—202).—The investigations were undertaken with the object of elucidating a method for the detection and, if possible, estimation of minute traces of impurity, particularly of aqueous vapour, in nitrogen and the rare gases. They are based on the observations of Franck and Hertz (A., 1916, ii, 461), according to which an electron formed in the neighbourhood of a point cathode in a pure gas can lead to a strong ionisation, and consequent variation in the current, which, however, is irregular in occurrence, owing to the infrequency of the phenomenon. On the other hand, the presence of minute amounts of electronegative substances, such as oxygen, oxides of nitrogen, or water, causes an increase in the current, owing to the production of electrons at the cathode. Such a gaseous mixture, however, does not behave in a stable manner, the phenomena being complicated by the occurrence of slow chemical changes, which cause gradual alterations in the strength of the current, in accordance with the nature of the chemical processes. With a pure gas, the current rises initially, owing to the liberation of inherent impurities by the heat, but falls when the maximum of impurity has been passed. In an impure gas, on the other hand, more strongly electronegative products (such as nitric oxide) may be readily formed, thus causing a decrease in the current, which subsequently rises after partial or complete absorption of the impurities by the electrodes.

The apparatus, which is operated in duplicate, consists of a 2-litre globe furnished with an aluminium plate and a molybdenum point as electrodes, the current being provided by an alternating current high-tension transformer. In spite of somewhat considerable individual variations, the same characteristics are exhibited by both sets of apparatus. The electrodes need to be replaced frequently, as they are attacked by the impurities (oxygen and aqueous vapour). The pressure of the nitrogen is 700 mm. The sources of error are fully discussed, and it is shown that the differences due to heating effects are invariably smaller than those due to impurities. The pure nitrogen is obtained from the compressed gas by absorption of oxygen and subsequent desiccation, the last traces of oxygen and aqueous vapour being removed by passage over finely divided tantalum (which has been completely freed from gases) at 1000°. Such nitrogen, with a constant alternating tension of 4320 volts, gave a current–time curve which rises to a maximum in the first three minutes, and sinks more or less pronouncedly subsequently. 10^{-4} Ampere may be regarded as mean value for the current in pure nitrogen. With this current, a dark space of a few tenths of a millimetre surrouunds the point enclosed by a violet band, from which pass brush discharges; if

oxygen is now admitted, the discharge shrinks progressively until it can only be observed with a lens. With increasing oxygen content, the minimum current becomes progressively smaller, and the rise in the time-current curve occurs after a longer period.

The maximum current strength depends in some way on the oxygen content. The time-current curves for mixtures containing oxygen, in contrast to those for pure nitrogen, exhibit a steep rise after a time. Obviously, the oxygen is gradually consumed, possibly by formation of nitric oxide, which is removed by the molybdenum or other oxidisable part of the apparatus; such removal is not, however, quantitative, and minute traces of oxygen remain, which raise the current strength above the normal value. The mixture in which the greatest rise was observed contained about $5 \cdot 10^{-4}$%. Since measurements with similar vessels agree to within ±10%, the oxygen content can be measured (up to $5 \cdot 10^{-5}$%) after calibration of the apparatus with mixtures of known composition. In a similar, but less simple, manner, the content of aqueous vapour can be estimated. The appearance of the point discharge is more considerably modified by water vapour than by oxygen. The time-current curves, in contrast to those of mixtures containing oxygen, exhibit a definite and less defined minimum, which gradually disappears with increasing water-vapour content, and, in particular, shows a gradually rising branch, the current values for which with mixtures poor in aqueous vapour lie above those for pure nitrogen, and appear to lead asymptotically to a final value. The processes on which these curves depend are obviously very complicated, owing to the dissociation of water vapour. With slight modifications, the experiments can be extended to the rare gases; the sensitiveness is greater in these cases, but the phenomena are generally similar. The presence of hydrogen in nitrogen to the extent of 0·1% or more can be detected with certainty by means of the time-current curves, but the slight elasticity of the hydrogen molecules renders the method less sensitive. Apart from its analytical application, the method appears suitable for the investigation of the affinity of various substances at different temperatures for aqueous vapour, the dependence of the activity of reducing substances on temperature and state of division, and the after-glow of active nitrogen.

H. W.

Chemical Affinity of the Inactive Gases. FRANZ SKAUPY (*Zeitsch. Physik*, 1920, **3**, 408—411).—The indifference of the inactive gases is explained by the assumption that in all cases where an opportunity is presented for the formation of an inactive gas compound, there is at the same time an opportunity for the other constituents in the mixture to react and form much more stable molecules.

J. F. S.

Solubility of Graphite in Molten Iron. RUDOLF RUER and JULIUS BIREN (*Zeitsch. anorg. Chem.*, 1920, **113**, 98—112).—The

solubility of graphite in Swedish iron has been determined by heating the iron with graphite until saturated, and then pouring the molten metal into a metal tube so that it was cooled too rapidly for the dissolved graphite to separate. The metal was then dissolved in nitric acid (D 1·18) and the graphite determined in the usual way. Estimations were made at temperatures from 1152° to 2500°. Above 2500° approximate determinations show that the solubility continues to increase up to 2700°. The solubility curve of graphite in molten iron is linear from 1152° to 1700°, when it bends slightly at first and with increasing temperature more markedly away from the concentration axis. Examination of sections of the chilled metal showed graphite, cementite, and austenite, but no further crystalline substance. The concentration of the graphite eutectic which lies at 1152° is 4·25% carbon, that of the cementite eutectic which lies at 1145° is 4·30% carbon. The thick liquid which is formed when graphite and molten iron are in contact, with rising temperature, is due to the dissolved carbon, and the only action of the increased temperature is that it increases the solubility of the carbon in iron. J. F. S.

Properties of Potassium Arseno-thiosulphate: Structural Formula of Trithionic Acid. JULIUS VON SZILÁGYI (*Zeitsch. anorg. Chem.*, 1920, **113**, 75—84).—Potassium arseno-thiosulphate is prepared by adding a solution of 37·24 grams of crystallised sodium thiosulphate in 60 c.c. of water to a solution of 4·95 grams of arsenious oxide in 35 c.c. of hydrochloric acid (D 1·06) and 11·18 grams of potassium chloride in 30 c.c. of water at 3°. Three volumes of 96% alcohol are added to the mixture, when the double salt is precipitated. It is rapidly filtered and washed with alcohol and ether. It is a pure white compound, which is not very stable in the moist condition; it is amorphous, and is very soluble in water, slightly soluble in 50% alcohol, and insoluble in absolute alcohol, ether, and chloroform, D_4^{18} 2·292. When quite dry, it may be preserved, but when moist, even with chloroform or ether it becomes yellow. When the dry salt is heated, it decomposes according to the equation $2K_3As(S_2O_3)_3 = As_2S_3 + 3K_2SO_4 + 3SO_2 + 3S$; on keeping or boiling a solution of the salt it decomposes according to the equation $2K_3As(S_2O_3)_3 \rightleftharpoons As_2S_3 + 3K_2S_3O_6$. Attempts to prepare corresponding sodium and rubidium salts failed. The general relationships of the complex arsenic, bismuth, and antimony thiosulphates are considered (see Hauser, A., 1903, ii, 487), and it is shown that the existence and properties are influenced by the character of the tervalent element. In any given series of compounds the solubility increases in the order potassium, rubidium, cæsium, barium, sodium. The author deduces the structural formula of trithionic acid from the decomposition of potassium arseno-thiosulphate, which can only take place thus:

$$(KO\cdot SO_2\cdot S)_3As\quad As(S\cdot SO_2\cdot OK)_3 = As_2S_3 + 3KO\cdot SO_2\cdot S\cdot SO_2\cdot OK,$$

which gives trithionic acid the persulphide formula. J. F. S.

Figures Produced by Crystallisation of Potassium Dichromate. MASAMICHI KIMURA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 173—178).—When a solution of potassium dichromate is allowed to evaporate on a glass plate, crystallisation first starts at the boundaries of the solution, the crystals being built up inwards, but at a certain stage, the solution having become supersaturated, a different form of crystal growth suddenly starts in the central portion and proceeds with great rapidity. The crystalline deposit thus formed has the appearance of much-branched seaweed. By allowing the solution to evaporate on a gelatin film the rate of growth of this crystalline form was much reduced and its observation was facilitated. The phenomenon may be explained by supposing that, before crystallisation, the molecules of the solute, in virtue of their electric fields, combine to form molecular aggregates of increasing complexity as the solution becomes supersaturated. The paths traced out by the rapidly growing tree-like crystals may be taken as an indication of the distribution of these aggregates just before the solution begins to crystallise. E. H. R.

Investigation by means of *X*-rays of the Crystal Structure of Sodium Chlorate and Sodium Bromate. N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 644—653).—*X*-ray photographs were taken by the method described in a previous paper (A., 1919, ii, 108), using the finely powdered, crystalline substance. The length of the edge of the elementary cube cell, which contains four molecules, is $6{\cdot}55 \,.\, 10^{-8}$ for sodium chlorate and $6{\cdot}74 \,.\, 10^{-8}$ for the bromate. The unit cell being divided into eight small cubes, four of these cubes, chosen tetrahedrally, each contain one molecule, and the sodium and halogen atoms are situated on non-intersecting diagonals of the four cubes. The three oxygen atoms are grouped round a halogen atom. The distance between an oxygen atom and a neighbouring halogen atom is approximately one-seventh of the parameter of the lattice. E. H. R.

Investigations on the Salt Character of Lithium Hydride. KURT MOERS (*Zeitsch. anorg. Chem.*, 1920, **113**, 179—228).—Experimental details are given for the preparation of lithium hydride from lithium and hydrogen. To decide whether lithium hydride has the characteristics of a salt or no, the action of mercury on lithium hydride has been studied, and it is shown that the action is a decomposition, and not a solution, which points to the fact that lithium hydride is a salt. Investigation of the appearance, crystal form, density, heat changes, and specific heat and the determination of the various constants, and comparison of these with the corresponding constants for the alkali haloids all point to the salt character of the hydride. The following constants have been determined: density, 0·816; molecular volume, 9·77; heat of formation, 21,600±250 cal.; $Li + H_2O = LiOH + \frac{1}{2}H_2 + 52723 \pm 200$ cal.; $LiH + H_2O = LiOH + H_2 + 31110 \pm 50$ cal. The electrical conduc-

tivity has been determined with both direct and alternating current. The direct current experiments show a very large increase in conductivity with increase in temperature, but on account of polarisation which occasioned subsidiary changes a temperature–conductivity curve could not be constructed. With alternating current it is shown that the conductivity increases with increasing temperature until it reaches values of the same order as that of sulphuric acid of maximum conductivity. The temperature-coefficient of the conductivity shows a maximum at 550°. Galvanic polarisation could be detected, and its changes followed and measured. With direct current the products of the electrolysis could be isolated. The presence of hydrogen was proved by the increase in pressure during electrolysis in a vacuum, and metallic lithium was found on the cathode. From these facts and others it is practically certain that in the electrolysis of lithium hydride, hydrogen is liberated at the anode, and this represents the first instance in which hydrogen appears as a negatively charged ion. It is therefore shown that lithium hydride is to be regarded as a salt in which lithium constitutes the kation and hydrogen the anion, and hydrogen is to be regarded as an extremely weak acid. J. F. S.

Halogen Silver Ammoniates. WILHELM BILTZ and WILHELM STOLLENWERK (*Zeitsch. anorg. Chem.*, 1920, **114**, 174—202).—XI. (see *Zeitsch. anorg. Chem.*, 1919, **109**, 132). The apparatus of Hüttig (see this vol., ii, 195) was used. Freshly precipitated silver haloids are necessary, since these lose their activity on keeping. The existence of $AgCl,3NH_3$ and $2AgCl,3NH_3$ was confirmed, and a new compound, $AgCl,NH_3$, with dissociation pressures previously given for $2AgCl,3NH_3$ was obtained. The sesqui- and mono-ammoniates form mixed crystals above 30°. The existence of the compounds $AgBr,3NH_3$, $2AgBr,3NH_3$, and $AgBr,NH_3$ was confirmed, as well as that of the compounds $AgI,3NH_3$, $2AgI,3NH_3$, AgI,NH_3, and $2AgI,NH_3$. All the iodides form mixed crystals. The heats of formation were calculated from Nernst's formula $\log p = -Q_0/4\cdot57T + 1\cdot75 \log T + aT + 3\cdot3$ as follows (values of Q_0): $AgCl,3NH_3$, 9·16 Cal.; $AgCl,1\frac{1}{2}NH_3$, 10·52 Cal.; $AgCl,NH_3$, 11·11 Cal.; $AgBr,3NH_3$, 8·64 Cal.; $AgBr,1\frac{1}{2}NH_3$, 9·95 Cal.; $AgBr,NH_3$, 10·65 Cal.; $AgI,3NH_3$, 6·92 Cal.; $AgI,1\frac{1}{2}NH_3$, 7·25 Cal.; AgI,NH_3, 8·56 Cal.; $AgI,2NH_3$, 7·05 Cal.; $AgI,\frac{1}{2}NH_3$, 11·59 Cal.

The values of the constant a in the equation were found to be:

	$3NH_3$.	$2NH_3$.	$1\frac{1}{2}NH_3$.	NH_3.	$\frac{1}{2}NH_3$.
AgCl ...	−0·0025	—	−0·0015	−0·0015	—
AgBr ...	−0·0028	—	−0·0020	−0·0015	—
AgI ...	−0·0050	−0·0050	−0·0050	−0·0030	−0·0010

Conclusions on the affinities are drawn from the temperatures at which the dissociation pressures reach 100 mm. in all cases; these are in the order AgI, AgBr, AgCl. J. R. P.

Compounds of Ammonia with Metallic Calcium, Strontium, and Barium. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Zeitsch. anorg. Chem.*, 1920, **114**, 241—265).—A descrip-

tion of the method of preparation of strontium and barium by the method of Guntz (A., 1906, ii, 669) is given. All the alkaline-earth metals form hexammines, $M(NH_3)_6$. The values of Q_0 (see preceding abstract) were found from the tension curves to be: $Ca(NH_3)_6$, 10·32 Cal.; $Sr(NH_3)_6$, 9·91 Cal.; $Ba(NH_3)_6$, 9·65 Cal. The reaction $M(NH_3)_6 = M(NH_2)_2 + 4NH_3 + H_2$ occurs rapidly with barium, slowly with calcium. The identical behaviour of the metal atom and ion is pointed out. This may indicate that the presence of the two valency electrons in the atom has no influence on the absorption, or that the metal is composed of ions and free electrons.

J. R. P.

Basic Exchange in Silicates. III. E. RAMANN and H. JUNK (*Zeitsch. anorg. Chem.*, 1920, **114**, 90—104).—In continuation of previous work (A., 1917, ii, 468; 1919, ii, 154), the formation of magnesium permutite by the action of magnesium salts on ammonium, sodium, and potassium permutites has been studied. As in other cases, the reaction is ionic, and there is no evidence of physical adsorption. Pure magnesium permutite could not be obtained, not more than half of the bases present in the original permutite being displaced by magnesium. The whole of the ammonium in ammonium permutite could not be displaced by treatment with carnallite or kainite solutions. Mixed salt solutions decompose the permutite to some extent, especially solutions containing magnesium or ammonium. This observation may have some bearing on the decomposition of natural silicates, which cannot always be adequately accounted for by the action of water and carbonic acid.

E. H. R.

Liberation of Gas from Cold-worked Metals during Recrystallisation. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **114**, 278—280).—On heating a drawn copper wire in a vacuum, gas was evolved, the rate of evolution being greatest between 200° and 300°. At this temperature, the alteration of structure of the cold-drawn wire is also most rapid. The evolved gas gave the spectra of carbon monoxide and dioxide. Electrolytic iron showed in the first heating a maximum rate of evolution of gas at 530—600°; in the second heating at 610—650°. The spectrum of the gas showed the lines of hydrogen and carbon monoxide. A sublimate of lead was obtained from the iron. This is observed only when the metal has been cold-worked before heating in a vacuum.

J. R. P.

The Relative Firmness of the Combination of Sulphurous Acid with Ammonia and Mercury. OTTO RUFF and ERICH KRÖHNERT [with HANS JULIUS BRAUN] (*Zeitsch. anorg. Chem.*, 1920, **114**, 203—208).—The precipitate obtained from mercuric chloride and excess of ammonia dissolves when sulphur dioxide is passed through the liquid, and crystalline compounds of mercuric oxide with ammonia and sulphur dioxide are obtained on evaporation under reduced pressure. If sulphur dioxide is first added

and then ammonia, an insoluble compound containing sulphur dioxide and ammonia is slowly deposited. The reactions were found to be: (*a*) $HgCl_2 + 2H{\cdot}SO_3H + 4NH_3 = Hg''(SO_3{\cdot}NH_4)_2 + 2NH_4Cl$, (*b*) $NH_2Hg''Cl + H{\cdot}SO_3H = Hg''Cl(SO_3{\cdot}NH_4)$, in acid solutions. With excess of ammonia, a mixture of $Hg''(SO_3NH_4){\cdot}OH$, a white, insoluble powder, and $Hg''SO_3,NH_3$ or $Hg{<}{}^{SO_2-}_{NH_3}{>}O$, white needles, is precipitated:

$$Hg''(SO_3NH_4)_2 + NH_3 = Hg''SO_3,NH_3 + (NH_4)_2SO_3.$$

In presence of large amounts of ammonium chloride, one of the sulphonic groups is eliminated:

$$Hg''(SO_3NH_4)_2 + NH_4Cl + NH_3 = NH_3Cl{\cdot}Hg{\cdot}SO_3NH_4 + (NH_4)_2SO_3.$$

The compound, $NH_3Cl{\cdot}Hg{\cdot}SO_3NH_4$, forms long, white, transparent needles. $2N$-Potassium hydroxide converted this into yellow Hg_2O,SO_3,NH_3 or $O{<}{}^{Hg-SO_2}_{Hg{\cdot}NH_3}{>}O$. Concentrated ammonium hydroxide forms a solution, which appears to contain $Hg(NH_3)_4SO_3$; liquid ammonia forms $Hg(NH_3)_4SO_3$, as a white powder and ammonium sulphite.

In acid solution the sulphur, which receives a negative charge from oxygen, and in alkaline the nitrogen, which receives a negative charge from hydrogen, possess a strong tendency to complex formation, and in ammoniacal solution, complexes corresponding to mercurammonium sulphites are formed. J. R. P.

Compound Formation and the Electromotive Behaviour of Cerium in its Alloys with Iron and Zinc. FRITZ CLOTOFSKI (*Zeitsch. anorg. Chem.*, 1920, **114**, 1—23).—The author has applied Dolezalek's theory of binary mixtures (A., 1913, ii, 482) to the study of the binary alloys of cerium with zinc and iron respectively, and with its help has been able to demonstrate the presence of compounds in these alloys. For the preparation of the alloys, pure cerium was not available, but a metal was used containing cerium metals 97·0% (Ce 92·5%), iron 1·46%, silicon 0·88%, carbon 0·35%. Cerium–iron alloys containing from 3·9% to 84·1% of cerium, and cerium–zinc alloys containing from 26·6% to 92·7% of cerium, were prepared, and the potential difference between the alloy and pure cerium was determined in each case. It is shown on theoretical grounds that the concentration–potential difference curve in the case of a simple binary alloy, without compounds, has a logarithmic form, but if a compound is present in the alloy, a rapid increase of potential should take place at the concentration corresponding with the composition of the compound. When more than one compound is formed, the curve takes a horizontal course after the rise corresponding with the first compound, to rise again for the second compound. The curve for the iron–cerium alloys indicates the existence of a compound, CeFe, and also of a second compound, $CeFe_6$, but the composition of the latter is to some extent uncertain. The cerium–

zinc alloys show the presence of two compounds, Ce_4Zn and Ce_2Zn. The velocity constants of formation of the compounds were also calculated with the help of the theory. The constant for CeFe is given as $K=10^{10}$, whilst for the cerium–zinc alloys the constants are of the order $K_{Ce_4Zn}=4\cdot10^{77}$ and $K_{Ce_2Zn}=10^{57}$. E. H. R.

Oxidising Action of Ceric Sulphate. A. BENRATH and K. RULAND (*Zeitsch. anorg. Chem.*, 1920, **114**, 267—277).—In the oxidation of tartaric acid by ceric sulphate in presence of sulphuric acid, small quantities of didymium sulphate are without influence on the velocity. Formic acid is produced, $C_4H_6O_6 + 8Ce(SO_4)_2 + 2H_2O = 3CO_2 + HCO_2H + 4Ce_2(SO_4)_3 + 4H_2SO_4$. Addition of sulphuric acid strongly retards the reaction. Oxalic acid is oxidised to carbon dioxide,

$$C_2H_2O_4 + Ce(SO_4)_2 = 2CO_2 + Ce_2(SO_4)_3 + H_2SO_4.$$

Sulphuric acid and normal sulphates retard this reaction. Complex formation was not observed. The oxidation of anthracene is strongly accelerated by addition of sulphuric acid. The oxidation of hydrazine occurs according to the equation $2N_2H_4 + 2Ce(SO_4)_2 = N_2 + (NH_4)_2SO_4 + Ce_2(SO_4)_3$. Hydroxylamine gave nitrogen and nitrous oxide (69—73%). Sodium thiosulphate was converted into tetrathionate, $2Na_2S_2O_3 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + Na_2SO_4 + Na_2S_4O_6$. Sulphurous acid forms equivalent amounts of sulphuric and dithionic acids; hypophosphorous acid is oxidised to phosphorous acid. Photo-oxidation of formic acid, methyl alcohol, and acetic acid is retarded by sulphuric acid.

J. R. P.

The Purification and Testing of Aluminium. FRANZ MYLIUS and WERNER MYLIUS (*Zeitsch. anorg. Chem.*, 1920, **114**, 27—64).—Experiments were made on the further purification of technical "pure" aluminium, which may contain Al 99·58%, Fe 0·18%, Si 0·22%, C 0·02%. When such a metal crystallises slowly, practically pure aluminium first crystallises, the impurities crystallising last in the eutectic. Such aluminium can be granulated by stirring the metal during crystallisation, and by extracting the granules with dilute hydrochloric acid, most of the iron can be removed. By repeating this process three times, a metal was prepared containing Al 99·9%, Fe 0·02%, Si 0·2%, C 0·01%, the loss being 50%. Purification can also be effected by partly melting the metal and separating the less pure liquid portion from the purer aluminium crystals, but the process is tedious and the yield of pure metal is low.

Experiments were made with the object of devising a test for determining the probable behaviour of technical aluminium when exposed to atmospheric influences. It was shown that aluminium of the highest obtainable purity is but slightly attacked by 20% hydrochloric acid and by other corrosive agents.

[See, further, *J. Soc. Chem. Ind.*, 1921, 150A.] E. H. R.

System and Constitution of Derivatives of Molybdic Acid. L. FORSÉN (*Compt. rend.*, 1921, **172**, 215—217).—The author considers that all the known molybdates may be derived from two acids, molybdic acid, $H_6Mo_3O_{12}$, and metamolybdic acid, $H_{12}Mo_2O_{12}$, and to molybdic acid he assigns the constitutional formula $O{<}{\scriptstyle\begin{matrix}MoO(OH)_2\cdot O\\ MoO(OH)_2\cdot O\end{matrix}}{>}MoO(OH)_2$. To explain the formation of anhydrides, four spacial representations are admitted. A new *anhydride*, $H_4Mo_3O_{11}$, has been obtained in a crystalline form, and two potassium trimolybdates, having the composition

$$K_2Mo_3O_{10},3H_2O.$$

W. G.

Metallographic Investigation of the System Tungsten-Lead. SUEKICHI INOUYE (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 43—46). —Alloys of lead and tungsten containing up to 30% of the latter were prepared and investigated by the thermal method. At 1300°, the highest temperature used, lead dissolves a maximum of 30% of tungsten. The temperature of primary crystallisation could not be detected with less than 5% of tungsten. Tungsten crystallises first, and the eutectic appears to be practically pure lead. No evidence of the formation of a compound on the lead side could be found, and it is improbable that there could be one on the tungsten side, on account of the low boiling point of lead.

E. H. R.

Preparation of Uranium Compounds in the Pure State. ERNST WILKE-DÖRFURT (*Wiss. Veroffentl. Siemens-Konzern*, 1920, **1**, 143—146; from *Chem. Zentr.*, 1921, i, 170—171).—In connexion with an investigation of the catalytic activity of uranium compounds, an attempt was made to obtain a highly purified uranium oxide, U_3O_8, from some residues of cleveite which had been used for the extraction of helium. A solution of the nitrate which had been purified from the rare earth metals and thorium by oxalic acid, and from extraneous heavy metals by hydrogen and ammonium sulphides, yielded an oxide, which was not free from alkali. In the opinion of the author, the presence of the latter is due to co-precipitation of uranate, and not to adsorption, and can therefore be avoided by reduction of the uranium. By suitable regulation of the action of ammonium sulphide, it is found possible to precipitate uranous instead of uranyl sulphide, and this substance does not show any tendency to retain alkali; the latter, if absorbed, can be removed by double precipitation, and avoided by working with smaller quantities. The sulphide is readily converted into uranous chloride, which is transformed through the hydroxide into the nitrate; the latter is oxidised by nitric acid to uranyl nitrate, which is purified by being crystallised from water, and then converted into the oxide, U_3O_8, in which the presence of traces of alkali cannot be detected spectroscopically. The author avoids the frequently recommended crystallisation of uranyl nitrate from ether, since, on the one hand, the product so obtained is not

free from alkali, and, on the other, the explosive tendency of the ethereal solution renders it unsuitable for working with very valuable material. H. W.

The Existence of a Gaseous Hydride of Thorium. ALBERT KLAUBER and JULIUS MELL VON MELLENHEIM (*Zeitsch. anorg. Chem.*, 1920, **113**, 306—316).—An alloy of thorium and magnesium was prepared by heating thorium oxide, ThO_2, with two to two and a-half times its weight of magnesium powder for forty-five minutes to a dull red heat in a stream of hydrogen. A blackish-brown to grey product was obtained, which, when powdered in a mortar, gave a characteristic odour of thorium hydride. The gas was formed when the alloy was treated with water or dilute acids, and had a tendency to ignite spontaneously. To identify the gas, the method used by Paneth (A., 1920, ii, 758) for identifying lead and bismuth hydrides was used, the gas being passed through a heated Marsh tube, when a deposit of thorium was obtained, which was identified by a number of characteristic reactions. The thorium is at first deposited in the form of a brown ring, which, on further heating, becomes dark grey with a metallic appearance, indicating the existence of two modifications of thorium. The hydride is very unstable, and is produced in greatest amount at a temperature of 15—20°. The composition of the hydride could not be determined. The gas can be condensed with liquid air. Its radioactivity is very slight. E. H. R.

Antimony Pentasulphide (Sulphur Auratum). F. KIRCHHOF (*Zeitsch. anorg. Chem.*, 1920, **114**, 266. See A., 1920, ii, 693).—Some varieties of commercial sulphur auratum contain less than 8% (0—2%) of sulphur readily extracted by solvents. These are probably obtained by the reaction $Na_3SbS_4 + SbCl_3 = Sb_2S_4 + 3NaCl$. J. R. P.

Metallographic Investigation of the System Antimony Sulphide–Silver Sulphide. KOSUKE KONNO (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 51—54).—The liquidus curve for the system antimony sulphide–silver sulphide shows a maximum at a point corresponding with 42% of silver sulphide, indicating the formation of the compound Sb_2S_3,Ag_2S, which is known in the form of the mineral miargyrite. The microscopic appearance of a section of this composition is quite homogeneous. Two eutectics are formed, between the compound and antimony sulphide at 462° with 22% Ag_2S, and between the compound and silver sulphide at 464° with 72% Ag_2S. No mixed crystals are formed in either case. E. H. R.

Metallographic Investigation of the System Antimony Sulphide–Lead Sulphide. DAIDZI IITSUKA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 61—64).—The thermal investigation of the antimony sulphide–lead sulphide system shows the existence of four compounds, each of which corresponds with a known mineral. The

maximum on the liquidus curve corresponds with the compound $2PbS,Sb_2S_3$, jamesonite, the melting point of which is 672°. This compound reacts with excess of antimony sulphide at 610° to form the compound $3PbS,2Sb_2S_3$, warrenite, which exists in two modifications with a transition temperature at 510°. This compound, in turn, reacts with antimony sulphide to form PbS,Sb_2S_3, zinckenite. In reguli containing between 41% and 51% of PbS the last two compounds co-exist as separate phases. The last-named compound forms a eutectic with antimony sulphide at 428°, containing 14% PbS. The first compound, $2PbS,Sb_2S_3$, also reacts with lead sulphide at 590° to form the compound $5PbS,2Sb_2S_3$, corresponding with the mineral boulangerite. This compound exists in two modifications with a transition point at 468°, and forms a eutectic with lead sulphide at 557° containing 78% of PbS. E. H. R.

Some Alkali Antimony Thiosulphates. JULIUS VON SZILÁGYI (*Zeitsch. anorg. Chem.*, 1920, **113**, 69—74).—The preparation and properties of stibio-thiosulphates of sodium, potassium, rubidium, barium, calcium, and strontium are described. The method of preparation consists in adding a solution of antimony trioxide in hydrochloric acid (D 1·12) to a solution of sodium thiosulphate and the chloride of the metal concerned at low temperatures, about 3°. The formation is represented by the equations: $SbCl_3 + H_2O = SbOCl + 2HCl$; $SbOCl + 2HCl + 3Na_2S_2O_3 = 3NaCl + H_2O + Na_3Sb(S_2O_3)_3$. The salts in all cases, except those of sodium, calcium, and strontium, may be crystallised at low temperatures and are precipitated by the addition of 96% alcohol. *Sodium stibio-thiosulphate*, $Na_3Sb(S_2O_3)_3$, is extremely soluble, and has not been obtained in the solid condition; all attempts to obtain the solid salt brought about decomposition according to the equation

$$2Na_3Sb(S_2O_3)_3 = 3Na_2S_2O_3 + Sb_2OS_2 + 4SO_2.$$

Potassium stibio-thiosulphate, $K_3Sb(S_2O_3)_3$, forms silk-like, needle-shaped crystals very similar in appearance to asbestos. It is very soluble in water, and on diluting the solution a very slight turbidity is produced which points to the presence of the complex ion, $Sb(S_2O_3)_3'''$. On boiling a solution decomposition occurs, forming the orange-red compound, Sb_2OS_2, as in the case of the sodium compound. On heating the crystals above 100° the decomposition $2K_3Sb(S_2O_3)_3 = Sb_2S_3 + 3K_2SO_4 + 3SO_2 + 3S$ takes place. This compound is shown to have the constitution $Sb(S{\cdot}SO_2{\cdot}OK)_3$. The rubidium salt is similar in all respects to the potassium salt. *Barium stibio-thiosulphate*, $Ba_3[Sb(S_2O_3)_3]_2$, is not very stable at the moment of precipitation; it is white, but speedily becomes yellow, and finally very deep yellow in colour, due to decomposition. The strontium and calcium salts exist for only a very short time in solution, and have not been isolated. J. F. S.

Metallographic Investigation of the System Bismuth-Selenium. NAOJIRO TOMOSHIGE (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 55—60).—A thermal investigation of the bismuth–selenium system

led to the following results. The compound Bi_2Se_3 is indicated by a maximum on the liquidus curve; the compound forms white prisms melting at 688°. It mixes with excess of bismuth in the liquid state, and on cooling crystallises out until the temperature reaches 602°, at which point a reaction takes place between the compound and bismuth with formation of the β-form of a new compound, BiSe, the reaction taking place with development of heat. On further cooling the compound BiSe crystallises out down to 422°, the transition point, at which it changes into the α-form. The final eutectic temperature on the bismuth side is practically the melting point of bismuth, 267°. On the selenium side of the diagram the compound Bi_2Se_3 forms a homogeneous liquid with 14% of selenium, which at 604° deposits the compound. With more than 51% of selenium two layers are formed, the above homogeneous liquid being in equilibrium with a solution of selenium containing 9% of bismuth. On cooling, Bi_2Se_3 is deposited until one liquid layer disappears; the other then deposits the compound, and finally crystallises as a eutectic at 161°. E. H. R.

Metallographic Investigation of the System Bismuth Sulphide-Antimony Sulphide. YASUYO TAKAHASHI (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 47—50).—Mixtures of bismuth and antimony sulphide were examined by the cooling method, and the liquidus and solidus curves plotted. The two sulphides form a complete series of mixed crystals. At its melting point bismuth sulphide dissociates to the extent of about 1·5% into bismuth and sulphur.
E. H. R.

Chemical and Galvanic Activity Boundaries of the Copper-Nickel, Palladium-Copper, and Palladium-Silver Mixed Crystals. LEO NOWACK (*Zeitsch. anorg. Chem.*, 1920, **113**, 1—26. Compare Tammann, A., 1919, ii, 398).—Mixed crystals of nickel and copper, palladium and copper, and palladium and silver have been prepared, and the limits of the chemical activity of these crystals, which in each case cover the whole range of compositions, have been determined by a study of the rate of reaction of sodium hydroxide, alkaline hydrogen peroxide solutions, an alkaline solution of tartaric acid, ammonium persulphate, silver nitrate, silver sulphate, copper sulphate, copper nitrate, mercuric cyanide, nitrate, and chloride, respectively, with the various mixed crystals. The evolution of oxygen from the crystals when used as anode in the electrolysis of various salts has been studied, and the general electromotive behaviour of the various alloys determined. It is shown that in the case of palladium–copper alloys the activity boundary toward various chemical reagents lies at 2/8 mol. palladium; in certain cases this value is not quite reached, and in one single case it is slightly exceeded. The same boundary is found for the copper–nickel alloys, except with sodium persulphate and mercuric cyanide, where the boundary 4/8 mol. nickel is obtained. In the action of silver sulphate and mercuric nitrate on the nickel–

copper alloys the activity persisted up to 6/8 mol. nickel; this activity is, however, variable with temperature, and consequently has not the same significance as the other activity boundaries. A comparison of the results of Tammann (*loc. cit.*) for gold–copper alloys with the present results for nickel–copper alloys or palladium–copper alloys shows that the activity boundary toward solutions containing active sulphur, and weak oxidising agents, is practically the same in all three cases. The same is also true for the precipitation of palladium from a solution of palladium chloride. On the other hand, the precipitation boundary of silver from silver salts lies at $\frac{1}{8}$ mol. gold in gold–copper alloys, but at $\frac{2}{8}$ mol. palladium in palladium–copper alloys. In the precipitation of mercury by gold–copper alloys the precipitated mercury diffuses into the alloy and destroys the space-lattice, whereby copper atoms which are not on the surface become exposed to the action of the reagent. For this reason alloys which are extremely poor in copper precipitate mercury, and there is no activity boundary. Since the relationship of palladium to mercury is much less than that of gold to mercury, this complication does not occur with the palladium–copper alloys, and in this case the activity boundary lies sharply at $\frac{2}{8}$ mol. palladium. The electrometric determination of the *P.D.* of copper–nickel alloys shows that the whole of the series of alloys have the same *P.D.* as pure copper. Anodic evolution of oxygen occurs with palladium–copper alloys from 1·0 to 0·28 mol. palladium, with palladium–silver alloys from 1·0 to 0·48 mol. palladium, and with copper–nickel alloys from 1·0 to 0·48 mol. nickel. The current–potential curves show the same decomposition voltage for all alloys of the above-mentioned compositions. The voltage at which a stronger and continuous opposing current flows is the same as that with palladium for all palladium–copper and palladium–silver alloys up to $\frac{4}{8}$ mol. palladium, whilst for nickel–copper alloys up to $\frac{4}{8}$ mol. nickel it is the same as that of nickel. The hydrogen solubility in the alloys of palladium with silver and copper has been determined, and it is shown that in the palladium–silver alloys the solubility at first increases with decreasing palladium content, and then decreases, and at $\frac{1}{2}$ mol. palladium, hydrogen ceases to dissolve. The same results are found with palladium–copper alloys, except that there is no initial increase in the solubility. J. F. S.

Chemistry of the Platinum Metals. I. Existence of Bivalent Ruthenium Compounds. Heinrich Remy (*Zeitsch. anorg. Chem.*, 1920, **113**, 229—252).—After a general discussion of the valency of the platinum metals, it is shown that only one compound, ruthenocyanic acid, is known in which the ruthenium exists in the bivalent condition. The author has examined the blue solutions of ruthenium compounds obtained by the action of reducing agents on ruthenic compounds and other derivatives of a higher state of oxidation. The method consisted in titrating solutions of ruthenic chloride with dilute sodium amalgam until the

sepia-brown colour of the solution changed to clear blue. Further additions of amalgam did not affect the colour, but there was a precipitation of metallic ruthenium. All experiments were carried out in an atmosphere of carbon dioxide. The experiments show that in the blue solution ruthenium is present for the most part in the bivalent condition, but it appears to be impossible to effect a complete conversion of all the ruthenium into the bivalent condition without at the same time reducing some of it to the metallic condition. There are indications that a proportion of the bivalent ruthenium ions is converted into univalent ruthenium ions. The action of a number of reagents on the blue solution has been investigated: cold sodium hydroxide gives a brown coloration which, if the solutions are concentrated, becomes a brown precipitate, soluble in hydrochloric acid to form a blue solution, but if only a trace of air is admitted the solution is green; hot sodium hydroxide gives a dark brown precipitate which is soluble in 10% hydrochloric acid with the formation of a yellowish-brown solution; ammonia gives a greyish-black precipitate soluble in hydrochloric acid to a blue solution and soluble in excess of ammonia to a dark violet solution; hot ammonium carbonate gives a dark green coloration; iodine solutions are decolorised in the presence of acid. The whole of the reactions of bivalent ruthenium solutions show that in this valency stage ruthenium compounds are excessively unstable. J. F. S.

Mineralogical Chemistry.

The Formation and Chemical Structure of Coal. F. FISCHER and H. SCHRADER (*Brennstoff-Chem.*, 1921, **2**, 37—45).—In the peatification of plant residues the cellulose is acted on by bacteria, disappearing in time, being converted into carbon dioxide and water. This results in an increase in the relative amount of lignin. This course of events can be followed in peat. The methoxyl group in the lignin is hydrolysed with the production of methyl alcohol, or is reduced to the methyl group. The methyl alcohol may have been further reduced to methane. By saponification of the acetyl group the neutral lignin is converted into a phenolic, alkali-soluble substance, humic acid. From the humic acids the humins are obtained by condensation, with the loss of water. Further loss of water, carbon dioxide, and possibly methane at normal temperatures gives coal and lignite. The benzene structure of the original lignin is retained throughout the formation. A comparison of the behaviour of lignin and cellulose with different reagents indicates that it is the former, and not the latter, which must be regarded as the mother substance of coal. W. P.

Exchange of Ions on the Surface of Minerals. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1920, **113**, 149—162).—The author has measured the potential of galena, litharge, zinc blende, graphite, magnetite, iron pyrites, manganese silicide, and orthoclase against the normal hydrogen electrode,

$$Zn \mid 2N\text{-}ZnSO_4 \text{ soln.}, Pb \mid PbCl_2(\text{sat.}) \mid, Cu \mid CuSO_4 \mid, \text{ and } Ag \mid Ag_2SO_4(\text{sat.}),$$

under various conditions of polarisation, and from the results has shown that minerals, such as sulphides and silicates, suspended in aqueous solutions exchange their less noble kations for the more noble hydrogen kation. This hydrogen charge then protects them from exchange with metal ions, which are less noble than the hydrogen ion. In the case of the sulphides, the exchange takes place rapidly, but with silicates extremely slowly. The present results confirm the work of Rubens (*Sitzungsber. K. Akad. Wiss. Berlin*, 1917, **1**, 47), who found that binary salt crystals reflected and absorbed certain ultra-red rays very strongly, and in order that this could occur, it is necessary that the points of crystal lattice must be occupied by ions, a demand which the present work substantiates. The present work also explains the adsorption of very small quantities of radioactive substances and the presence of small quantities of noble metals in the compounds of less noble metals. J. F. S.

Bementite and Neotocite from Washington: Identity of Caryopilite with Bementite. J. T. PARDEE, E. S. LARSEN, jun., and GEORGE STEIGER (*J. Washington Acad. Sci.*, 1921, **11**, 25—32).—Bementite occurs over a wide area in western Washington, where with other manganese minerals it forms large rock masses associated with limestones in metamorphic rocks. The fresh material is light grey or brownish-grey, and is compact and tough; H 6, D 3·106. Under the microscope, it is seen to consist of a felted aggregate of transparent fibres and plates with micaceous cleavage. It is decomposed by hot acid, and is readily fusible to a black glass. Analysis I is of material (from the Olympic Range) isolated by means of heavy liquids. This is compared with previous analyses of bementite from Franklin Furnace, New Jersey (G. A. Koenig, 1887, and A., 1910, ii, 220), and the average molecular ratio of the three analyses is $40·7MnO,34·8SiO_2,24·1H_2O$, or nearly $8MnO,7SiO_2,5H_2O$. This composition is not essentially different from that of the Swedish caryopilite (A. Hamberg, 1889), and the optical characters are also in agreement

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MnO_2.
I.........	39·92	1·32	—	4·15	41·58	—
II.........	37·15	2·58		—	37·00	2·03

	CaO.	MgO.	H_2O-.	H_2O+.	CO_2.	Total.
I.........	0·40	4·46	0·49	7·90	—	100·22
II.........	2·86	2·82	14·07		2·10	100·61

Neotocite occurs as veinlets in the bementite of the Olympic

Range. It is brown to black, with resinous lustre and conchoidal fracture; brittle (H 4) and optically isotropic. Analysis II is compared with earlier analyses of this mineral; they suggest a ratio $R''O:SiO_2$ near 1:1, with variable amounts of water.

L. J. S.

Augite from Vesuvius and Etna. HENRY S. WASHINGTON and H. E. MERWIN (*Amer. J. Sci.*, 1921, [v], **1**, 20—30).—Crystals of augite from scoria and vesicular leucite-tephrite from the crater of Vesuvius gave I; the material analysed enclosed some glass, leucite, and magnetite; D 3·242, refractive index β 1·700—1·711. Loose crystals from ashes and tuffs at Monti Rossi, Etna, gave II (III after deducting 4% of magnetite); D 3·373, refractive indices of the material analysed near α 1·704, β 1·711, γ 1·732.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO
I.	47·60	1·52	6·01	3·17	4·59	0·13
II.	47·89	2·02	3·55	4·17	5·98	0·20
III.	50·09	2·11	3·71	1·47	4·96	0·21

	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	21·52	14·43	0·70	0·76	0·08	100·51
II.	21·49	13·40	0·70	0·01	0·21	99·62
III.	22·48	14·01	0·73	0·01	0·22	100·00

Anal. I is very close to one given by A. Lacroix (*Compt. rend.*, 1917, **165**, 211) of pyroxenite, consisting almost entirely of granular augite, from Monte Somma, Vesuvius. The reason why apparently the same material should form floating crystals as well as such a granular aggregate is discussed in connexion with theories of differentiation by gravitation and by fractional crystallisation.

Anal. II corresponds with the molecular percentages $CaMgSi_2O_6$ 70·0, $CaFeSi_2O_6$ 16·5, $CaSiO_3$ 1·5, $(Mg,Fe)Al_2SiO_6$ 7·0, $Na(Fe,Al)Si_2O_6$ 5·0. The Etna augite is compared with that from Stromboli (A., 1918, ii, 271). General remarks are made on the imperfections of mineral analyses; in the previous analyses of these augites, titanium and alkalis were not estimated. L. J. S.

Analytical Chemistry.

A Soxhlet Apparatus for Extraction with Warm Solvents. LEO SOEP (*Chem. Weekblad*, 1921, **18**, 97).—The vapour of the solvent is made to pass through a worm coiled against the inside wall of the extractor before escaping to the condenser.

S. I. L.

The Importance of Adsorption in Analytical Chemistry. IV. The Adsorption of Alkalis by Cellulose. V. The Adsorption of Salts of the Alkali and Alkaline Earth Metals and of Alkaloids by Filter Paper. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 46—56. Compare this vol., ii, 19, 123).—IV. Cotton wool or filter paper was shaken with a standard alkali solution, which, after equilibrium was reached, was titrated with acid in presence of dimethyl-yellow. No difference was observed in the alkali content of the solution poured or filtered off from the cellulose and that expressed from the cellulose. For sodium and potassium hydroxides, the quantities adsorbed by 1 gram of cellulose are directly proportional to the end concentration of the solutions up to a strength of $4N$. For sodium hydroxide solutions having end concentrations between $4N$ and $6N$, the quantity taken up is constant. When the end concentration increases above $6N$, the amount taken up increases suddenly, remaining constant at the new value until the end concentration reaches $8N$. There is thus no adsorption, in the true sense, at all. With barium hydroxide, the amounts taken up, within the limits of solubility in water, were proportional to the square roots of the end concentrations. Sodium and potassium carbonates were not taken up at all. In presence of traces of other alkalis, the quantity of ammonia taken up from aqueous solution is constant and independent of the concentration, but if no other alkali or if acid be present, none is taken up.

V. Neither calcium nor barium salts are taken up by filter paper; with the former, slight negative adsorption was observed, and traced to the calcium content of the ash. With sodium chloride solutions, slight negative adsorption of the chlorine ion was found. With ammonium chloride, no adsorption occurs of either ion, and the same was found for the nitrates, sulphates, iodides, and chromates of the alkali metals. With the chromates in acid solution, no adsorption occurs, but, after long keeping, gradual oxidation of the paper sets in.

For the determinations with alkaloid salts, estimation with permanganate was adopted, the factor being determined for each alkaloid. With morphine hydrochloride, no adsorption occurred, but quinine hydrochloride and strychnine nitrate were both taken up in small quantities, the amounts being found to be in exact agreement with the adsorption equation $x/m = ac^{1/n}$, where x/m is the quantity adsorbed per gram of filter paper, c is the end concentration of the solution, and a and $1/n$ are constants.

S. I. L.

Apparatus for Titration with Alkali Hydroxides. A. BESSEMANS (*J. Pharm. Belg.*, 1920, **2**, 495; from *Chem. Zentr.*, 1920, iv, 702).—The alkali hydroxide in the burette is protected from the action of atmospheric carbon dioxide, since air can only enter the apparatus after passage through potassium hydroxide solution (10%).

H. W.

The Determination of Hydrogen-ion Concentration by the Colorimetric Method and an Apparatus for Rapid and Accurate Work. ERNEST VAN ALSTINE (*Soil Sci.*, 1920, **10**, 467—479).—An apparatus is described for use where a large number of determinations of hydrogen-ion concentration of various solutions are necessary. It is adapted for use with the double-tube standards of Gillespie (*Soil Sci.*, 1920, **9**, 115). The essential part of the new apparatus is an eyepiece, which is shown in detail in the original. W. G.

Estimation of Iodides in the Presence of Iodates. V. THÜRINGER (*Bull. Soc. Chim. România*, 1920, **2**, 73—77).—For the estimation of iodates in the presence of iodides, 0·2 gram of the substance dissolved in water is added to a solution containing 1·5 gram of potassium iodide and 5 c.c. of dilute sulphuric acid, and the iodine liberated is titrated with $N/10$-sodium thiosulphate solution. For the estimation of the iodide, a known volume of $N/60$-iodic acid, in excess of that required to decompose all the iodide, is added, the solution is acidified with sulphuric acid, and boiled until the whole of the free iodine has been driven off. It is then cooled, and the residual excess iodic acid is estimated as described above. From these two titrations, the amount of iodide present in the original mixture can be calculated.
W. G.

Estimation of Hydrogen Sulphide in Natural Waters. É. CHRÉTIEN and H. VANDENBERGHE (*Ann. Chim. anal.*, 1921, [ii], **3**, 19—23).—One litre of the water, having a normal alkalinity due to carbonates, is treated with 20 c.c. of saturated barium chloride solution, and filtered out of contact with the atmosphere; 510 c.c. of the filtrate are then added to 10 c.c. of $N/100$-iodine solution and 0·1 gram of potassium iodide, 10 c.c. of $N/100$-thiosulphate solution are added, and the excess of the latter is titrated with $N/100$-iodine solution. W. P. S.

Microchemical Identification of Gaseous Ammonia as Hexamethylenetetramine Picrate. C. KOLLO and (MLLE) V. TEODOSSIU (*Bull. Soc. Chim. România*, 1920, **2**, 100—102).—The reagent used is a 40% solution of formaldehyde saturated first with picric acid and then with hexamethylenetetramine picrate. On exposing a drop of this solution on a microscope slide in an atmosphere containing a trace of ammonia, characteristic microscopic crystals of hexamethylenetetramine picrate are deposited. W. G.

Behaviour of Neutral Ammonium Citrate in certain Phosphate Solutions. H. E. PATTEN and G. H. MAINS (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 235—237).—Ammonium citrate, when added to a hydrochloric acid solution of a phosphate baking powder, prevents the precipitation of calcium phosphate on the addition of ammonia; the calcium phosphate is converted into calcium citrate, and at P_H values below 5·0 the calcium citrate is

kept in solution. At P_H values between 5·0 and 7·0 the precipitation of calcium citrate is very slow, but at 7·1 there is immediate formation of a gelatinous precipitate of calcium citrate. W. P. S.

Electric Oven for Use in Lockemann's Modification of the Marsh Apparatus for the Estimation of Arsenic. L. BIRCKENBACH (*Chem. Zeit.*, 1921, **45**, 61—62. Compare A., 1905, ii, 353).—A small oven or furnace is described for use in place of the ordinary Bunsen burner employed to heat the Marsh arsenic tube; it consists of a block of kieselguhr containing a channel for the tube and fitted with a heating spiral (nickelchrome wire) and a cover, the latter being made in two pieces. The author recommends the use of a granulated zinc–copper alloy (zinc, 500 grams; copper, 0·635 gram) in the reaction flask; this alloy yields a very steady current of hydrogen. W. P. S.

Colorimetric Estimation of Arsenic in the Urine and Blood of Persons Treated with Salvarsan. KURT SCHEFFLER (*Zeitsch. angew. Chem.*, 1921, **34**, 5—7).—The sample (for example, 100 c.c. of urine) is evaporated to one-fifth of its volume, 25 c.c. of a mixture of sulphuric and nitric acids (1 : 4) are added, the evaporation continued until a syrup is obtained, and this syrup is heated in a Kjeldahl flask with a further quantity of the acid mixture until a clear, colourless solution is obtained and all the nitric acid has been expelled. The solution is diluted with 25 c.c. of water, mixed with 75 c.c. of Bettendorf's reagent (stannous chloride dissolved in hydrochloric acid, D 1·123), the mixture boiled, and, after thirty minutes, the brown coloration due to arsenic is compared with standards containing known amounts of arsenic. The method is trustworthy for quantities of arsenic of not less than 0·04 mg. per 100 c.c. of urine. W. P. S.

The Detection of Sodium and Potassium Ions in the Presence of Magnesium Ions. Simplified Method. EUGÈNE LUDWIG and (MLLE) HÉLÈNE SPIRESCU (*Bul. Soc. Chim. România*, 1920, **2**, 78—82).—The metals of the group calcium, strontium, and barium are removed by precipitation with ammonium carbonate or oxalate, and the filtrate is evaporated to dryness and the residue ignited. One portion of the residue is examined for magnesium in the usual manner. For the detection of potassium, a drop of a solution of copper acetate and lead acetate in acetic acid is placed on a microscope slide. A drop of a solution of sodium nitrite is added and a particle of the ignited residue. The appearance of a black precipitate of cubic crystals of the compound, $K_2CuPb(NO_2)_6$, indicates the presence of potassium. For the detection of sodium a particle of the ignited residue is added to a drop of a concentrated solution of potassium carbonate on a slide and the liquid is evaporated to dryness. A drop of a solution of potassium pyroantimonate is added, and the appearance of a characteristic, crystalline precipitate of sodium pyroantimonate indicates the presence of sodium. W. G.

Application of *p*-Nitroaniline to the Standardisation of Sodium Nitrite Solutions. William H. Bell (*Chem. Met. and Eng.*, 1920, **22**, 1173; from *Chem. Zentr.*, 1921, ii, 94).—*p*-Nitroaniline (3·4517 grams) is washed into a 600 c.c. beaker and dissolved in a warm mixture of concentrated hydrochloric acid (10 c.c.) and water (100 c.c.), the solution being cooled subsequently to about 15°. The volume of the solution should be about 350 c.c. Sodium nitrite solution (7·0 grams per litre, about $N/10$) is added drop by drop with continuous stirring. If the solution is exactly $N/10$, 25·0 c.c. of it are required. After addition of 22 or 23 c.c., the solution is tested for free nitrous acid by starch-iodide paper. The method is more rapid and convenient than that recommended by Lunge.

H. W.

The Precipitation of Zinc with Chromium. Toyokichi Yasui (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 65—67).—The precipitate of chromium hydroxide, from a solution of a chromium salt, formed on addition of ammonia in presence of ammonium chloride is always contaminated with zinc if this is present in solution. Quantitative experiments were made, in which the ratio of Cr_2O_3 : ZnO in solution was varied within wide limits, and it was shown that the proportion of zinc hydroxide carried down by the chromium hydroxide increased with the proportion of ZnO present in solution. With a ratio Cr_2O_3 : ZnO equal to 1 : 11, the weight of ZnO found in the precipitate was one and a-half times the amount of Cr_2O_3 actually present. Three precipitations are necessary to obtain chromium hydroxide approximately free from zinc.

E. H. R.

New Modification of the Electrolytic Estimation of Copper. F. G. Hawley (*Eng. and Min. J.*, 1920, **110**, 162—165; from *Chem. Zentr.*, 1920, iv, 664—665).—The results obtained in the electrolytic estimation of copper are influenced by the presence of various components of the mineral, such as arsenic, antimony, bismuth, selenium, and molybdenum, which are completely or partly precipitated with the copper. These metals seldom occur in considerable quantity in copper ores, but are frequently present in small amount and accumulate markedly in the flotation concentrates. In general, their deposition commences after the bulk of the copper has been precipitated, and advantage may be taken of this peculiarity for their analytical detection. Slight or no co-precipitation occurs with 0·2—0·3% of arsenic, but with larger amounts a few tenths or 1% of this metal remains in solution, the remainder being precipitated with the copper. The latter is coloured pale grey by smaller amounts, darker by larger quantities. The behaviour of antimony resembles that of arsenic. Molybdenum is more frequently present in copper ores than is generally assumed. In the electrolytic estimation of copper, its behaviour is similar to that of arsenic and antimony. If only present in small amount, its deposition can be prevented by the addition of a small

quantity of a chloride; thus 1 mg. of sodium chloride prevents the precipitation of 6 mg. of molybdenum without affecting the precipitation of the copper. The presence of small amounts of the metal imparts a chocolate-brown colour to copper which, with larger quantities, becomes steel-blue to black. If the above impurities are only present to the extent of 0·10—0·15%, the copper may be obtained in the pure condition by solution from the cathode and re-deposition. Bismuth is precipitated completely with copper; with small quantities, the copper has a tile-red colour and exhibits black spots and stripes, whilst with larger amounts the whole precipitate is dark. Selenium and tellurium are deposited at the beginning of the electrolysis, so that an early occurrence of a dark coloration shows the presence of these elements. In the presence of bismuth, copper cannot be purified by repeated precipitation.

A modified method for the electrolytic estimation of copper is proposed. The sample (1—3 grams) is treated with sodium hydrogen sulphate (about 1 gram), ammonium sulphate (1 gram), and sulphuric acid (70%, 5 c.c.); nitric acid saturated with potassium chlorate (5 c.c.) is added, followed after one to two minutes by a further 10 c.c. of the reagent. The mixture is left in a warm place for a time, and subsequently heated until the bulk of the nitric acid is driven off; the sulphuric acid is then evaporated, and the residue is heated until it becomes pasty. Any iron which may be present is transformed by this treatment into anhydrous ferric sulphate, which is insoluble in concentrated, slightly soluble in dilute sulphuric acid. Water (1 c.c.) is added, followed by 50 c.c. of a solution containing ammonia (2 litres), water (4 litres), and ammonium nitrate (100 grams); after thorough stirring, the mixture is heated to boiling for a few seconds, cooled slightly, treated with ammonia (5 c.c.), and filtered. The precipitate is washed once with a little water, then with a little ammonia (1:1), and finally with water. The greater part of the copper is present in the filtrate, the remainder being retained with the impurities by the iron precipitate. The solution is boiled until most of the ammonia is expelled, and acidified when cold with sulphuric acid (3 c.c.) and nitric acid (3 c.c.). The remainder of the copper is brought into solution by treatment of the precipitate with dilute nitric acid, and reprecipitation of the iron by ammonia in the presence of a few drops of potassium cyanide solution (2%). This, together with the hydroxide precipitate, is treated in the rapid electrolysis apparatus with 0·2 ampère for twenty-five to thirty-five minutes, when the copper is deposited quantitatively at the cathode, whilst the impurities remain in the precipitate. The small quantity of copper is brought into solution by reversing the current, the main copper solution is added, and electrolysis is effected with 1—1·5 ampères. A further quantity of iron must be added if the specimen contains less than five times as much of this metal as of impurities, but the procedure is seldom necessary. Molybdenum is not removed in this manner, and, should it be present, it is necessary to introduce a

small quantity of a soluble lead salt before addition of the ammoniacal liquid. The particular action of the individual reagents is described. Test analyses show that the method, which in spite of the many individual operations is simple and rapid, gives accurate results. H. W.

Volumetric Analysis. OTTO SASSE (*Pharm. Zeit.*, 1920, **65**, 559, 688).—Methods are described for the volumetric estimation of mercuric chloride (titration with potassium iodide solution), chloroform (decomposition with potassium hydroxide and determination of the chloride formed), and lead salts (titration with an excess of potassium dichromate solution and iodometric determination of the excess). The method given for mercuric chloride may be used for the analysis of mercuric chloride tablets after the red colouring matter has been destroyed by treatment with chlorine. W. P. S.

Decomposition of Iron Oxides. F. LETEUR (*Ann. Chim. anal.*, 1921, [ii], **3**, 16—19).—Practically all mineral iron oxides may be dissolved readily by heating them at 65° in closed vessels with concentrated hydrochloric acid, particularly if the latter is saturated with hydrogen chloride just before use. The pressure developed is not great, and ordinary flasks may be used with little risk of breakage. W. P. S.

The Hydrogen-ion Concentration at which Iron is Precipitated from Hydrochloric Acid Solution by Ammonia, Sodium Hydroxide, and Hydrogen Sulphide. H. E. PATTEN and G. H. MAINS (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 233—235).—When a hydrochloric acid solution containing 0·03% of iron is treated with hydrogen sulphide, ammonia, or sodium hydroxide, the first appearance of a precipitate of ferrous sulphide or of colloidal ferric hydroxide occurs when the hydrogen-ion concentration is slightly above $P_H=3·3$. W. P. S.

Volumetric Estimation of Iron in the Presence of a Large Quantity of Hydrochloric Acid. R. MEURICE (*Ann. Chim. anal.*, 1921, [ii], **3**, 23—25).—Ferrous salt solutions containing a large quantity of hydrochloric acid may be titrated with permanganate solution if potassium bromide is added to the iron solution and a current of air passed through the latter during the titration; the air is then bubbled through a mixture of potassium iodide solution and starch. As soon as all the ferrous salt has been oxidised, the next drop of permanganate solution added liberates bromine, and this is carried over into the potassium iodide solution, where a blue coloration develops. W. P. S.

New Process for the Separation and Estimation of Iron and Manganese. C. KOLLO (*Bul. Soc. Chim. România*, 1920, **2**, 89—95).—When hexamethylenetetramine is added to a solution of a ferric salt, the whole of the iron is precipitated as ferric hydroxide in the cold, even in acid solution. With manganous salts, a

precipitate of manganous hydroxide is only obtained in boiling neutral solution. If a solution of the tetramine in alcohol is added to a concentrated aqueous solution of manganous sulphate and sulphuric acid in equimolecular proportions, the crystalline double *sulphate*, $MnC_6H_{12}N_4,2H_2SO_4$, is obtained.

For the estimation of iron and manganese in the presence of one another, the mixture of salts is dissolved in water, acidified, and the iron entirely oxidised to the ferric state by means of hydrogen peroxide. A 10% solution of hexamethylenetetramine is then added until the whole of the iron is precipitated as ferric hydroxide, which is collected, dried, ignited, and weighed as the oxide. The filtrate is evaporated to dryness, a little sulphuric acid is added to the residue, and the evaporation is continued, the manganese being weighed as its sulphate. W. G.

Detection and Estimation of Nickel and Cobalt. MOTOOKI MATSUI and TADASU NAKAZAWA (*Mem. Coll. Sci. Kyoto*, 1920, **4**, 265—271).—Nickel hydroxide reacts directly with a 1% alcoholic solution of dimethylglyoxime. In presence of other hydroxides, nickel may be detected by boiling the mixed hydroxides for a short time with excess of dimethylglyoxime solution, diluting considerably with water, cooling, and shaking with ether. On keeping, the nickeldimethylglyoxime floats up with the ether. Cobaltdimethylglyoxime may be detected in solution by adding a drop or two of yellow ammonium sulphide solution, when a very intense red colour is produced if cobalt is present. The test is very delicate when a large excess of dimethylglyoxime is used, but since ferrousdimethylglyoxime also gives a red colour, iron must not be present. Attempts to find an insoluble double compound of cobaltdimethylglyoxime were unsuccessful, although a double lead–cobalt compound was obtained by adding lead acetate to a solution of cobaltdimethylglyoxime, in the form of orange-yellow crystals.

Alkaline solutions of the dimethylglyoxime compounds of nickel and cobalt were successfully electrolysed quantitatively, the metal forming a well-adhering deposit from a dilute solution, less than 0·05 gram per 100 c.c. It is thus possible to separate nickel and cobalt in the usual way with dimethylglyoxime and estimate both metals by electrolysis. A 5—6% solution of sodium hydroxide is used as the electrolyte and a current of 3·5 amperes with a rotating electrode, the temperature being below 50°. E. H. R.

Iodometric Estimation of Chromic Acid. I. M. KOLTHOFF (*Zeitsch. anal. Chem.*, 1920, **59**, 401—415).—The statements made in a recent paper (A., 1919, ii, 300) have been confirmed. Volumetric thiosulphate solutions may be standardised, with an error of less than 0·1%, by means of purified potassium dichromate, bromate or iodate, iodine, cyanogen iodide, or oxalic acid. Potassium dichromate commonly contains free chromic acid, and should be recrystallised from water several times and dried at 120°.

J. H. L.

Detection of Methyl Alcohol in Spirits. F. Rabe (*Pharm. Zeit.*, 1921, **66**, 72).—When the morphine–sulphuric acid reagent is used for the detection of formaldehyde, resulting from the oxidation of methyl alcohol, care should be taken to expel all hydrochloric acid from the reagent if this is prepared by mixing morphine hydrochloride and sulphuric acid; the reagent itself soon develops a red coloration in the presence of hydrochloric acid. The resorcinol–sulphuric acid test is very sensitive for the detection of formaldehyde. W. P. S.

Detection of Methyl Alcohol in Spirits. G. Maue (*Pharm. Zeit.*, 1921, **66**, 114—115).—The resorcinol–sulphuric acid test mentioned by Rabe (preceding abstract) for the detection of formaldehyde resulting from the oxidation of methyl alcohol is not new, and, further, it is not characteristic of formaldehyde, the coloration being also given by the oxidation products of allyl alcohol, formic acid, tartaric acid, etc. W. P. S.

Cholesterolanæmia. I. Comparative Investigations of [Analytical] Methods with Particular Reference to Colorimetric Processes. Joh. Feigl (*Zeitsch. ges. exp. Med.*, 1920, **11**, 178—238; from *Chem. Zentr.*, 1921, ii, 97).—The author reviews the methods given in the literature and his own processes for the estimation of cholesterol, as a whole and as its component parts, in blood. He is led to the conclusions that the different colorimetric processes are trustworthy when accurately carried out, but contain many sources of error, and that the total cholesterol in the strictest sense cannot at present be estimated in this manner. The individual methods are not equal in value as judged from the pathological point of view, and further comparative investigations are necessary. Only small sections can be regarded as yielding practically useful values. H. W.

The Estimation of Dextrose in Blood and in Cephalorachidien Fluid. Al. Ionescu and V. Vargolici (*Bul. Soc. Chim. România*, 1920, **2**, 102—106).—The blood or fluid under examination is first defecated by the addition of a 20% solution of trichloroacetic acid. The filtrate obtained after defecation is neutralised by sodium hydroxide, and the dextrose present is estimated by its reduction of a solution of potassium ferricyanide (compare *ibid.*, 38). W. G.

Modifications of Bertrand's Method for Estimating very small Quantities of Sugar. L. Ambard (*Bull. Soc. Chim. Biol.*, 1920, **2**, 203—205).—The author advises heating the sugar solution with the copper reagents in a centrifuge tube immersed in a water-bath. The precipitated cuprous oxide is collected by centrifugalisation, washed, and dissolved in the tube by adding the ferric sulphate solution. J. C. D.

Estimation of Sugar in Wine. W. FRESENIUS and L. GRÜNHUT (*Zeitsch. anal. Chem.*, 1920, **59**, 415—457).—The authors consider that the present German official methods for the estimation of sugars in wine require revision, and should be replaced by a scheme of analysis which is described in detail in the present paper. [Compare *J. Soc. Chem. Ind.*, 1921, 158A.] J. H. L.

Reactions of Sugars and Polyatomic Alcohols in Boric Acid and Borate Solutions, with some Analytical Applications. G. VAN B. GILMOUR (*Analyst*, 1921, **46**, 3—10).—Polyatomic alcohols, sugars, and a large number of hydroxy-compounds combine with boric acid with the production of stronger acids. On the addition of an excess of mannitol to a boric acid solution, mannitoboric acid, $C_6H_{12}O_6{:}BOH$, is formed; this, with sodium hydroxide, yields a salt which is stable in acid solution, but is hydrolysed to sodium metaborate and mannitol in alkaline solution, the metaborate then combining with a further quantity of mannitol to form compounds like $NaBO_2,3C_6H_{14}O_6$.

A method for the estimation of lævulose is as follows. Ten c.c. of *M*/10-boric acid solution and 0·5 c.c. of 1% phenolphthalein solution are added to a weighed amount of mixed sugars (honey, etc.) containing lævulose, and the mixture is titrated with *N*/10-sodium hydroxide solution; the amount of lævulose equivalent to the volume of sodium hydroxide used is obtained from the table:

Lævulose. Gram.	*N*/10-NaOH. Cc.	Lævulose. Gram.	*N*/10-NaOH. Cc.
0·22	7·2	0·36	8·9
0·27	8·1	0·40	9·2
0·31	8·5	0·45	9·5

W. P. S.

The Identification of Sulphonic Acids in the State of their Salts formed with Aromatic Bases. C. F. VAN DUIN (*Rec. trav. chim.*, 1921, **40**, 99—102. Compare Ambler, this vol., i, 21; Ambler and Wherry, this vol., ii, 68).—The author finds that sulphonic acids may be identified, where necessary, by titrating their salts of aromatic bases with *N*/10-sodium hydroxide in the presence of phenolphthalein as indicator (compare Franchimont and Backer, this vol., i, 9). This method was satisfactorily applied to *aniline* and p-*toluidine toluene*-o-*sulphonates*, m. p.'s 218° and 203—204° respectively; *aniline* and p-*toluidine toluene*-p-*sulphonates*, m. p.'s 237° and 199—200° respectively; *aniline* and p-*toluidine* 2:6-*dinitro*-1-*toluene*-4-*sulphonates*, p-*toluidine sulphanilate*, *aniline naphthalene*-β-*sulphonate*, m. p. 267—268° (decomp.), and to *di*-p-*toluidine toluene*-2:4-*disulphonate*, m. p. 277° (decomp.). W. G.

Separation and Identification of Lactic Acid as Complex Ferric Sodium Lactate. K. A. HOFMANN (*Ber.*, 1920, **53**, [*B*], 2224—2226).—Details are given of the preparation of a very pale

green, complex *ferric sodium lactate*, $[Fe(C_3H_4O_3)_2]Na,2H_2O$. This loses water at 80°, is almost insoluble in water at 20°, is only slowly attacked by dilute ammonia, sodium hydroxide, sodium hydrogen carbonate, 15% acetic acid, 1% hydrochloric acid or tannic acid, and is almost tasteless. When heated at 300°, or exposed to sunlight, it evolves acetaldehyde.

To separate lactic acid from fermentation products in the form of this salt, the solution should be mixed with little more than the required amount of ferric chloride, rendered alkaline with sodium carbonate, acidified with acetic acid, and evaporated on a water-bath. The characteristic precipitate separates in the course of a few hours

Corresponding potassium and ammonium salts are less stable, and are only partly precipitated, whilst no lithium salt has been obtained. J. C. W.

Identification of Acetaldehyde and Formaldehyde in Organic Liquids and Mixtures by means of New, Extremely Sensitive, Colour Reactions. EMILIO PITTARELLI (*Arch. Farm. sperim. Sci. aff.*, 1920, **30**, 148—160).—Acetaldehyde may be detected by adding, to 25—30 c.c. of the approximately neutral liquid to be tested, successively five to six drops of saturated (about $N/10$) phenylhydrazine hydrochloride solution, saturated diazobenzenesulphonic acid, 25% sodium hydroxide solution, and 50% magnesium sulphate solution; the last may be omitted if the colour appears after addition of the alkali hydroxide. A crimson coloration results, this beginning to appear almost instantaneously, although the reaction is complete only after some minutes; with the magnesium hydroxide, this yields a violet lake. In absence of either acetaldehyde or phenylhydrazine, only a yellow coloration is produced, this remaining unchanged by formaldehyde or acetone. The reaction is capable of detecting 1 part of acetaldehyde in 350,000 parts of solution, or 1 part of phenylhydrazine in 70,000 parts of solution.

To detect formaldehyde, 25—30 c.c. of the liquid under examination are treated in order with five to six drops of saturated phenylhydrazine hydrochloride solution, 1% metol solution, 25% sodium hydroxide solution, and 50% magnesium sulphate solution; here, too, the last may be omitted if it is unnecessary. In presence of formaldehyde, a blood-red coloration is formed, this giving a blue lake with the magnesium hydroxide. The reaction is capable of detecting 1 part of formaldehyde in 1,000,000 parts of solution, 1 part of phenylhydrazine in 250,000 parts of solution, and 1 part of metol in 300,000 parts of solution.

The above reactions may be applied directly to organic liquids and mixtures, such as urine, wine, milk, spirits, beer, foods, etc. T. H. P.

New Apparatus for Quantitative Sublimation. A. V. FULLER (*Chem. Analyst*, 1920, **29**, 6—10).—The apparatus

consists of two parts, the heater and the condenser. The heater is a glass tube about 18 cm. in length and 16 mm. in diameter, which is slightly tapered and ground at one end to fit gas-tight (without a lubricant) into one end of the condenser, which is a glass tube about 15 cm. in length and 19 mm. in diameter. The other, closed end of the condenser is indented to more than half the length of the condenser, forming an inner tube, through which cooling water can be passed. This end of the condenser also carries a side-tube, which can be attached to a pump

The condenser is closed by a ground-in stopper, and weighed. It is then attached to the heater containing a weighed amount of the substance to be sublimed, a slow current of air (1·3 litres per hour) is drawn through the apparatus, and the heater is carefully heated, preferably by external electrical heating. At the end of the operation, the air current is stopped when the tubes are cold, the inner tube of the condenser is dried with alcohol and with ether, and the stoppered condenser is re-weighed. The accuracy obtainable depends on the temperature of volatilisation, the temperature of condensation, and the time and rate of flow of the air current. In three experiments with 0·6085 gram of camphor, 0·6610 gram of naphthalene, and 0·3415 gram of benzoic acid, the temperatures of volatilisation were 130°, 130°, and 145°, the temperatures of condensation 12°, 20°, and 20°, and the recoveries 99·34, 99·97, and 100·06% respectively. CHEMICAL ABSTRACTS.

Estimation of Santonin in Wormseeds. TATSUO KARIYONE and YÛSHIRO KIMURA (*Off. Gaz. Japan*, 1920, 760—761; *J. Pharm. Soc. Japan*, 1920, 927—940).—The method depends on the estimation of the saponification value, utilising the lactone formation. Ten grams of powdered *Artemisia Cina*, Berg., are treated with ether for three hours in a Soxhlet apparatus. After distilling off the solvent, the residue is boiled with 100 c.c. of 5% baryta water, acidified with dry carbon dioxide, and filtered. Eighty c.c. of the filtrate (8 grams of sample) are extracted with 20 c.c. of chloroform with addition of 10 c.c. of 15% hydrochloric acid, filtered, and then extracted three times with 10 c.c. of chloroform. After distilling off the solvent, the residue is dissolved in 30 c.c. of ethyl alcohol by heating, cooled, and neutralised with $N/10$-potassium hydroxide, using phenolphthalein as indicator, boiled for thirty minutes under reflux with 20 c.c. of $N/10$-potassium hydroxide, cooled, and titrated with S c.c. of $N/10$-hydrochloric acid with addition of 0·5 c.c. of phenolphthalein. If S' is the amount of the acid required for neutralising 20 c.c. of $N/10$-potassium hydroxide which has been boiled with 30 c.c. of ethyl alcohol, then $2·462(S'-S)/8$ gives the percentage of santonin. K. K.

Estimation of Urea in Blood. Actual State of the Question. M. LAUDAT (*J. Pharm. Chim.*, 1921, [vii], **23**, 5—15).—A full account of work on which two preliminary notes have been published (see A., 1920, ii, 645; this vol., ii, 70).

Estimation of Urea by Sodium Hypobromite. L. AMBARD (*Bull. Soc. Chim. Biol.*, 1920, **2**, 205—208).—A discussion of the technique of this method. A method for removing oxygen from the liberated gas is described. J. C. D.

Detection of Hydrogen Cyanide in Air. A. SIEVERTS and A. HERMSDORF (*Zeitsch. angew. Chem.*, 1921, **34**, 3—5).—A strip of filter-paper is dipped in a copper acetate–benzidine acetate solution and then exposed for seven seconds in the atmosphere to be tested; a blue coloration is obtained if the air contains 15 mg. or more of HCN per cubic metre. The reagent is prepared immediately before use by mixing equal volumes of copper acetate solution (2·86 grams per litre) and benzidine acetate solution (475 c.c. of cold saturated benzidine acetate solution and 525 c.c. of water). W. P. S.

A Direct Method for the Estimation of Dicyanodiamide in Cyanamide and Mixed Fertilisers. ROLLA N. HARGER (*J. Ind. Eng. Chem.*, 1920, **12**, 1107—1111).—The method depends on the precipitation of the dicyanodiamide with silver picrate; cyanamide and urea do not interfere, since they do not yield a precipitate with the reagent. In the case of mixed fertilisers, 20 grams of the sample are mixed with 50 c.c. of water, 100 c.c. of saturated barium nitrate solution are added, the mixture rendered alkaline with barium hydroxide, shaken for thirty minutes, diluted to 500 c.c., and filtered. To 200 c.c. of the filtrate are added 15 c.c. of 5% silver nitrate solution, the mixture is filtered if silver chloride forms, and then treated with 100 c.c. of saturated picric acid solution. The mixture is cooled at 0° for thirty minutes, the crystalline precipitate then collected on a weighed asbestos filter, washed with water saturated with the compound (a precipitate from a former analysis can be used for this purpose), then with ether, dried at 100°, and weighed. The weight found is increased by 0·0044 gram for each 100 c.c. of solution from which the crystals were filtered, and the result is divided by 5 to obtain the amount of dicyanodiamide. W. P. S.

Estimation of Aniline and its Titrimetric Diazotisation. TH. SABALITSCHKA and H. SCHRADER (*Zeitsch. anal. Chem.*, 1921, **34**, 45).—Aniline cannot be estimated quantitatively by precipitation with excess of a ferric salt or with formaldehyde, neither can it be accurately titrated with acid in presence of any known indicator. The statement in many text-books, that the red colouring matter of dahlias constitutes a suitable indicator for this purpose, is incorrect. Aniline may be titrated accurately with $N/1$-sodium nitrite solution, with the aid of potassium iodide–starch test paper as external indicator. The liquid should contain at least 2—3 mols. of sulphuric acid to 1 mol. of aniline, and be cooled with ice-water, whilst the nitrite solution is added a few drops at a time and later drop by drop until the nitrite reaction

persists for fifteen minutes. [See, also, *J. Soc. Chem. Ind.*, 1921, Mar.] J. H. L.

Methyl-red as Indicator in the Estimation of Alkaloids. A. EBERHARD (*Apoth. Zeit.*, 1920, **35**, 318—319; from *Chem. Zentr.*, 1920, iv, 659).—The applicability of methyl-red as indicator in alkaloidal estimations in the place of hæmatoxylin or iodoeosin is confirmed for methods similar to that of Herzog (*Apoth. Zeit.*, 1920, **35**, 216). H. W.

Estimation of Theobromine in Cocoa and its Products. RAYMOND V. WADSWORTH (*Analyst*, 1921, **46**, 32—37).—Ten grams of the substance are mixed with 3 grams of magnesium oxide and 14 c.c. of water, dried partly, but not completely, and then boiled under a reflux apparatus for thirty minutes with 150 c.c. of tetrachloroethane. The mixture is filtered while hot, and the residue again extracted with tetrachloroethane. The united extracts are distilled to reduce the volume to about 5 c.c., and this residual liquid, when cold, is mixed with 70 c.c. of ether. After eighteen hours, the precipitated theobromine is collected, washed with ether, dried at 100°, and weighed. To the weight obtained is added 0·004 gram to correct for the solubility of the precipitate in the 70 c.c. of ether. Cocoa beans require extraction with light petroleum to remove excess of fat previous to the estimation of the theobromine. W. P. S.

New Method for the Estimation of Histidine. W. E. THRUN and P. F. TROWBRIDGE (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 194—195).—The method is used in conjunction with the Van Slyke method, and depends on the absorption of bromine by histidine and cystine. A portion of the solution containing the bases of a coagulable protein is treated with bromide–bromate solution and hydrochloric acid, and, after fifteen minutes, the excess of bromine is titrated. Cystine is estimated separately in another portion of the solution by estimating the sulphur content. One molecule of cystine absorbs 10 atoms of bromine, whilst 1 molecule of histidine absorbs 2 atoms of bromine; there is some evidence, however, that the latter absorption somewhat exceeds 2 atoms of bromine. W. P. S.

Estimation of Morphine in Opium and certain of its Preparations. TRIFON UGARTE (*J. Pharm. Chim.*, 1921, [vii], **23**, 129—131).—One gram of powdered opium is heated on a water-bath for five minutes with 10 c.c. of 67% alcohol, the alcoholic solution then filtered, and the insoluble residue extracted three times with alcohol in a similar way. The united alcoholic extracts are evaporated, the residue dried at 100° for fifteen minutes, then dissolved in 5 c.c. of cold water, the solution filtered, and any insoluble substance extracted with successive quantities of water,

using 20 c.c. in all. The aqueous solution is evaporated, the residue dissolved in 2 c.c. of water saturated previously with morphine, 3 c.c. of $N/1$-ammonia solution, also saturated with morphine, and 10 c.c. of ether are added, and the mixture is agitated thoroughly; 20 c.c. of ether are next added, the mixture stirred, and, after thirty minutes, the crystalline precipitate of morphine is collected, washed with water saturated with morphine and ether, dried at 100°, and weighed. In the case of opium tincture, 10 c.c. of the sample are evaporated, the residue dried, extracted with cold water, and the estimation proceeded with as described. W. P. S.

The Separation of Ptomaines from Vegetable Alkaloids in Toxicological Examinations. AL. IONESCU (*Bul. Soc. Chim. România*, 1920, **2**, 82—89).—In an endeavour to find a ready method of distinguishing between vegetable alkaloids and ptomaines in the presence of one another, the author has examined the influence of certain enzymes on the ptomaines and on strychnine, coniine, and morphine as typical of three classes of alkaloids, and the influence of the ptomaines and the alkaloids on the activity of the enzymes. The material under examination was acted on for twenty-four hours by the enzyme under the optimum conditions, and the alkaloids and ptomaines then extracted by Dragendorf's method, using either benzene or amyl alcohol as solvents. Hydrolysing enzymes of the type of invertase and amylase have no action on the ptomaines, whilst pepsin weakens their reducing power without affecting their alkaloidal character. Tyrosinase and peroxydase destroy only the reducing power of the ptomaines. Neither the ptomaines nor the alkaloids affect the activity of the enzymes. Under the experimental conditions the vegetable alkaloids examined were not affected by any of the enzymes used. W. G.

Peru Balsam and its Adulteration. L. VAN ITALLIE (*Amer. J. Pharm.*, 1921, **93**, 24—26).—A sample of Peru balsam having the consistency of a thin syrup gave, on examination, D 1·146; acid number, 48·8; saponification number, 356; cinnamein content, 70%; saponification number of the separated cinnamein, 382. The high saponification numbers of the balsam and cinnamein indicated adulteration with an ester, and the presence of methyl phthalate was shown by the fluorescein test with resorcinol and sulphuric acid applied either to the balsam or the separated aromatic ester. Such adulteration of balsams may also be recognised by Dietrich's test (*Ber. Deut. pharm. Ges.*, 1908, 142). Benzoyl benzoate is also used as an adulterant, and its presence, although not indicated by the saponification number, may be shown by the fluorescein test or by Dietrich's test W. G.

Estimation of Uric Acid in Blood by Folin's Method. I. A. ZALESKI and (MISS) A. A. SACHNOVSKA (*Russ. Physiol. J.*, 1919, **2**, 14—35).—Experiments have been made to test the accu-

racy of the results yielded by Folin's method (Folin and Macallum, A., 1912, ii, 495; 1913, ii, 80; Folin and Denis, A., 1913, ii, 162, 444), which depends on comparison in a colorimeter of the intensities of the blue colorations obtained when the uric acid solution to be tested and a standard uric acid solution are treated with phosphotungstic acid in presence of an alkali. The authors suggest various modifications in the procedure. The magnesium–silver salt, in the form of which the uric acid is separated from the blood, is best decomposed, not by hydrogen sulphide, but by hydrochloric acid, the silver chloride being then removed by filtration from the uric acid solution; this alteration shortens the time required by the estimation very considerably. For determining the intensity of the blue coloration obtained with the phosphotungstic reagent, use is made of blue glasses previously standardised with the help of uric acid solutions of known concentrations. The method admits of the estimation of the amount of uric acid in 10 c.c. of blood with an error of at most 0·05 m. gram. T. H. P.

New Method for the Estimation of Uric Acid in Blood. ALEKSANDER OSEACKI (*Przeglad. Lekarski, Krakau*, 1920, **59**, No. 4; from *Chem. Zentr.*, 1921, ii, 97).—Serum (20—50 c.c.) is diluted with 4—14 times its volume of water and freed from albumin by treatment with uranyl acetate solution (1·5%, in volume equal to that of the serum). The precipitate is filtered, dissolved in a warm mixture of water (equal in volume to the filtrate), and $N/2$-sodium hydroxide solution, re-precipitated with $N/2$-acetic acid, and filtered whilst hot. Uric acid is separated in the usual manner from the combined and concentrated filtrates. H. W.

Apparatus for Estimating the Catalase Content of Milk. A. MACHENS and FR. CORDES (*Milch. Zentr.*, 1921, **50**, 25—27).—Two similar bottles are connected at their shoulder by a short tube fitted with a three-way tap; at the bottom of one bottle is a tubulure which is connected with a vertical graduated tube. This bottle is filled with water so that the level of the latter is at the zero mark on the tube. Fifteen c.c. of milk are placed in the other bottle, both are closed with stoppers, and the whole apparatus is placed for fifteen minutes in an oven heated at 37°, the three-way tap being turned so as to place both bottles in communication with the atmosphere. Five c.c. of 1% hydrogen peroxide are then added to the milk, the tap is turned to place the bottles in communication with each other, and the apparatus is kept at 37°. The evolution of gas increases the pressure in the apparatus, and this pressure is indicated by the water rising up the graduated tube. W. P. S.

Application of the Precipitometer and of an Apparatus for the Estimation of Catalase to the Study of the Course of Alcoholic Fermentation. K. SCHWEIZER (*Bull. Assoc. Chim. Sucr.*, 1920, **38**, 163—171).—For the measurement of yeast growth

in fermentation experiments the author recommends treating portions of the culture with sodium carbonate solution and centrifuging for five minutes at 2000 revs. per min. in a tube with a constricted graduated end (precipitometer). For the measurement of the gas evolved, an apparatus devised by Koestler (*Jahresb. Molkerei Ruetti*, 1909) for the estimation of catalase is recommended. J. H. L.

The Water-soluble Vitamin and the Substances Accelerating Fermentation. I. A Method for the Estimation and the Preparation of a Substance from Yeast and Rice Polishings which Accelerates Fermentation. SIGMUND FRÄNKEL and ERIK SCHWARZ (*Biochem. Zeitsch.*, 1920, **112**, 203—235).—Utilising the fact that extracts from yeast and rice polishings accelerate fermentation, the authors have worked out a method by means of which the accessory factor can be estimated. An active fraction from yeast is prepared in the following way. The yeast is extracted with 80% alcohol, and, after removal of the fats, is treated with basic lead acetate. The lead in the active filtrate is removed with hydrogen sulphide, and the filtrate further precipitated with mercuric chloride. The precipitate is then decomposed with hydrogen sulphide, freed from hydrochloric acid, and concentrated in a vacuum. The concentrated syrup is precipitated with picrolonic acid, which removes an inactive picrolonate, and the active substance is precipitated with phosphotungstic acid. The precipitate is decomposed with baryta and sulphuric acid, and concentrated in a vacuum. The sulphate of the active base thus obtained is twenty-two times more potent than the original alcoholic extract. S. S. Z.

A Microchemical Reaction of Pulmonary Epithelial Tissue. E. FAURÉ-FREMIET, J. DRAGOÏU, and (MLLE) DU VIVIER DE STREEL (*Bull. Soc. Chim. Biol.*, 1920, **2**, 166—170).—The test depends on the treatment of the tissue with a reagent containing formaldehyde and cadmium chloride. The presence of sulphur in the tissues causes a deposit of cadmium sulphide to be formed. J. C. D.

General and Physical Chemistry.

The Molecular Refraction Coefficient, its Additivity and its Use for Determining Constitution. III. Numerical Relationships in the Series of Polymethylene Compounds. FRITZ EISENLOHR (*Ber.*, 1921, **54**, [*B*], 299—320. Compare A., 1920, ii, 717; this vol., ii, 1).—In previous papers it has been pointed out that the "molecular coefficient of refraction," $M \times n_D^{20}$, is more sensitive to constitutive changes in the molecule than the generally employed molecular refraction, and values have been calculated for aliphatic and benzenoid compounds. In the present communication, polymethylene compounds are similarly considered, but, for the time being, the treatment is limited to the *trans*-isomerides which are in general obtained by Sabatier's method of hydrogenation in the presence of nickel. In contrast to the behaviour of benzenoid derivatives, in which the number of side chains appears to have more influence on the *E* value than their position, it is found with the *cyclo*-paraffins that the data are more affected by the location than by the number of side chains.

The author draws the conclusion that the refractive index in the form of the "molecular coefficient of refraction" can be used in this series for distinguishing between compounds of very closely allied structure. The differences between the observed values and those calculated for the individual components and linkings (*E* values) not only throw great light on the molecular structure, but also serve as criteria of the degree of purity of the substances. The natural expression of peculiarities of constitution is found in the index of refraction itself. The combination of this value with that of density in the usual molecular refraction is unfortunate, since the two constants are frequently influenced in much the same degree by constitutive changes, and the data thus obtained are only useful in explaining molecular structure in certain definite cases such as those in which conjugated double bonds, for example, are present.

H. W.

Spectro-chemistry of Benzene Derivatives. K. VON AUWERS [with ADELHEID FRÜHLING] (*Annalen*, 1921, **422**, 160—191).—The ordinary physical constants and the refractive indices for light of various wave-lengths have been measured for a large number of benzene derivatives of the following classes.

1. *Halogen Derivatives.*—In all cases the molecular refraction and dispersion are either normal or almost so, indications of exaltation being exhibited only with isolated compounds. Just as in aliphatic compounds, halogens and alkyl groups are here spectrochemically similar, entry of a substituent of either type into the benzene nucleus disturbing the optical neutralisation of the double linkings, and thereby enhancing the refractive and dispersive properties; this effect is less marked with the halogens than with the alkyls.

2. *Phenols and their Ethers.*—The results obtained confirm the observation that the differences in exaltation shown by isomeric phenols or by their ethers lie within very narrow limits. This absence of apparent relations between structure and physical constants is especially pronounced with the free phenols. Phenol ethers with two ortho-substituents differ markedly from the others, their boiling points, densities, refractive indices, molecular refractions, and molecular dispersions being lower than those of their isomerides; the differences are, indeed, so great that an *oo*-derivative may be recognised by means of any of these constants except the density. Just as with aromatic hydrocarbons and with the various classes of hydroaromatic compounds, so with the phenol ethers the exaltations are greatest with the symmetrical compounds, but the differences for the isomerides are not great. Other regularities, similar to but less marked than those occurring with the hydroaromatic alcohols, are also observed.

3. *Amines.*—With the four xylidines no relations of particular interest are detectable.

From these and previous results the general conclusion is drawn that, with increasing separation of the substituents the exaltations of benzene derivatives increase, whilst with increasing approximation they diminish.

Of the compounds considered the following are new.

Ethyl o-*chlorocinnamate* (compare Gabriel and Herzberg, A., 1883, 1123) has b. p. 160°/16 mm.

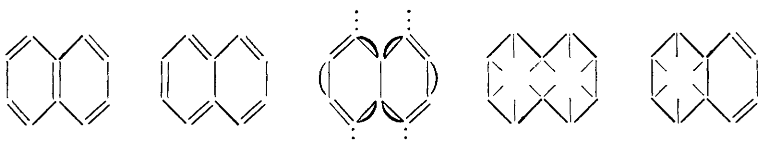
3 : 4 : 5-*Trimethylphenyl methyl ether* (*hemellithenol methyl ether*), $C_{10}H_{14}O$, crystallises in flat, oblique, shining prisms, m. p. 28—29°, b. p. 226—227°, the corresponding *ethyl* ether, $C_{11}H_{16}O$, being a colourless oil, b. p. 237—238°.

2 : 4 : 6-*Trimethylphenyl ethyl ether* (*mesitol ethyl ether*), $C_{11}H_{16}O$, forms a colourless oil, b. p. 217°. T. H. P.

Spectro-chemistry of Polynuclear Aromatic Compounds, and Constitution of Naphthalene. KARL VON AUWERS and ADELHEID FRÜHLING (*Annalen*, 1921, **422**, 192—230).—The results obtained for a large number of naphthalene derivatives indicate first, a general uniformity of the specific exaltations, and, secondly, dispersions which, in comparison with the highly augmented refractivities, are only moderately increased. These peculiarities, which are especially pronounced when the data obtained are compared with those of the benzene derivatives, confirm the rule that every class of compounds exhibits a typical spectro-chemical behaviour. In general, substituents are optically of little influence in the naphthalene series, but the halogens furnish an exception to this rule, the exaltations for the halogenated naphthalenes being only about one-half of that for the parent substance, although the dispersive power remains virtually unaltered. Whether highly unsaturated side-chains, such as the aldehyde or vinyl group, exert marked influence on the spectrochemical constants of naphthalene, is yet undecided. With the exception of 4-methoxy-1-naphthaldehyde, no derivative shows a higher exaltation than naphthalene

itself, so that the action of substituents in the naphthalene molecule, unlike that in the benzene molecule, is mostly depressive. It is noteworthy that in certain cases, particularly with esters, the dispersive power increases when the optical exaltation falls, so that refraction and dispersion seem to be mutually less dependent in the naphthalene series than in other groups of compounds. The influence of position is slight, although the optical exaltations are, on the average, somewhat higher with the β- than with the α-derivatives. In its optical constants acenaphthene corresponds perfectly with mono- and di-alkylnaphthalenes, the rule that the formation of a saturated ring does not alter the spectrochemical character being thus obeyed.

The bearing of these results on the various structures which have been proposed for the naphthalene molecule is discussed at length. The conclusion reached is that formula I, as originally interpreted



(I.) (II.) (III.) (IV.) (V.)

by Erlenmeyer, and also formulæ III, IV, and V are incompatible with the spectrochemical data. No choice is, however, yet possible between formula I, if this be taken to represent benzene with an unsaturated cyclic side-chain, and formula II, expressing a hydro-aromatic structure.

The following compounds containing two benzene nuclei, variously united, have also been examined: diphenylmethane, *p*-methyl-diphenylmethane, *m*-methylstilbene, diphenyl, *oo*-diphenol diethyl ether, diphenylene oxide, 9-methylfluorene, and fluorenone. Diphenylmethane behaves spectrochemically as a hydrocarbon of the benzene series, but when the chain between the two rings is unsaturated, as in methylstilbene, marked exaltation appears; the latter is also the case with diphenyl and its *oo*-diethoxy-derivative. Conversion of diphenyl into the tricyclic compounds, diphenylene oxide and fluorene, would be expected either to leave unaltered or to lower the exaltation of the parent substance, whereas the reverse is actually the case; fluorenone also exhibits unexpectedly high exaltation. Doubt is thus cast on the presence in the molecules of these tricyclic compounds of two true benzene nuclei; the double linkings of the two external rings no longer exist in a condition of optical neutralisation, but have assumed a more or less olefinic character, as in naphthalene and anthracene. That the ring-closure has really effected a fundamental change in the nature of the double linkings is indicated also by a comparison of the chemical properties of diphenylmethane with those of fluorene. In the former the methylene group between the two benzene rings is chemically indifferent, as it cannot be influenced by the mutually neutralised valencies of the benzene. In fluorene, on the other

hand, the hydrogen atoms of the uniting methylene group are highly reactive, being under the influence of two olefinic double linkings.

The following new compounds have been prepared. 2 : 3-*Diamyloxynaphthalene*, $C_{10}H_6(O·C_5H_{11})_2$, forms a very viscous, pale yellow oil, b. p. 229—230°/20 mm., and the isomeric 2 : 7-*compound*, slender, white needles, m. p. 75°, b. p. 236—237°/13 mm.

Ethyl 1-*methoxy*-2-*naphthoate*, $C_{14}H_{14}O_3$, forms a very viscous, colourless oil, b. p. 184—185°/14 mm. 3-*Methoxy*-2-*naphthoic acid*, $C_{12}H_{10}O_3$, forms small, pale yellow crystals, m. p. 133—134°, and its *ethyl* ester, a colourless, highly viscous oil, b. p. 208·5°/18 mm. or white crystals, m. p. about 18°; the *silver* salt was analysed.

m-*Methylstilbene*, $C_6H_5·CH⁚CH·C_6H_4Me$, prepared by the slow distillation of *m*-tolyl cinnamate (compare Anschütz, A., 1885, 1064), forms stout, white crystals, m. p. 52·5—53·5°, b. p. 206—207°/30 mm. T. H. P.

Optical Properties of some Crystals in the Long-wave Infra-red Spectrum. III. TH. LIEBISCH and H. RUBENS (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 211—220; see A., 1920, ii, 402).—The investigations previously described were extended to wurtzite, zircon, rutile, strontianite, and cryolite. The reflection capacity of wurtzite is less than that of regular zinc blende. The results with zircon were obtained with a better specimen than previous measurements, and gave higher reflection capacities than previously recorded. The high reflection capacities of rutile confirmed the high value of the dielectric constant of this mineral. J. R. P.

Criticism of Bohr's Theory of the Emission of Light. J. STARK (*Jahrb. Radioaktiv Elektronik*, 1920, **17**, 161—173. Compare Sommerfeld, Atombau, and Spektrallinien, Braunschweig, 1919).—A criticism of Bohr's theory of the emission of light in which it is shown that this hypothesis has been able to give, a quantitative deduction of the Balmer series formula and thereby the Rydberg constants; a quantitative representation of the effect of an electric field on the hydrogen series lines both with regard to the number and separation of the components, and also a deduction of the Zeeman triplets. These three services are obtained by means of three unsatisfactory assumptions, so that the solution of three difficulties has been obtained by the introduction of three new difficulties. The Bohr hypothesis proves the existence, in opposition to a number of observations, of the Doppler effect with canal rays, continuous spectra of atoms, the intimate structure of hydrogen and helium lines, the Zeeman effect of neighbouring line components in strong fields, whilst it does not indicate the dissymmetry of the intensity in the effect of the electric field on the hydrogen series lines. J. F. S.

The Corpuscular Spectra of the Elements. MAURICE DE BROGLIE (*Compt. rend.*, 1921, **172**, 274—275, 527—529).—A study of the corpuscular spectra of the elements from molybdenum to

barium shows the K rays of these elements transposed in the form of corpuscular rays. At the portion of the spectrum corresponding to the absorption band K of the elements there is a selective emission band of the photo-electric corpuscles with a sharp border at the side of the feeble energies. Thus the electrons from the commencement of the band possess the velocity corresponding with the quantum of the discontinuity of absorption of the X-rays, the band extending from the side of the greatest velocities. Thus in the corpuscular spectra of the elements all the characteristics of the X-ray spectra are found. W. G.

Action of the Red and Infra-red Rays on Phosphorescent Substances. MAURICE CURIE (*Compt. rend.*, 1921, **172**, 272—274).—The author has used simultaneously exciting and extinguishing radiations, the former from a mercury lamp with a glass-filter with nickel oxide, and the latter from an arc lamp with a glass-filter strongly charged with copper oxide. Under these conditions with phosphorescent zinc sulphide there can be observed, at the place where the infra-red rays are concentrated, a black spot on a background of bright luminosity. If the plate of sulphide is moved the brilliancy is reinforced, a luminous spot appearing, followed by a very dark trail behind the passage of the infra-red rays. This reinforcement of brilliancy varies in intensity and duration with the phosphorescent substance. With a fluorescent substance it is not possible to observe any spot or any variation in brilliancy at the place where the infra-red rays are concentrated. W. G.

Optical Rotation of Mixtures of Sucrose, Dextrose, and Lævulose. WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1921, **43**, 219—232).—The optical rotation of mixtures of sucrose, lævulose, and dextrose, dextrose and sucrose, lævulose and sucrose, and dextrose and lævulose has been measured for a series of mixtures of different concentrations at 25°, using either sodium light or the light from a mercury vapour lamp filtered through a No. 74 Wratten filter. It is shown that the specific rotations of dextrose and lævulose when mixed in equal proportions in solution (invert-sugar) are those which the sugars would have if each were present alone at a concentration equal to the total invert-sugar concentration. In other words, the angular rotation of an invert-sugar solution is equal to one-half the algebraic sum of the rotations of solutions of dextrose and lævulose of the same concentration. The specific rotations of dextrose and sucrose in mixtures of the two are those which the sugars would have if each were present alone at a concentration equal to the total sugar concentration. This relationship is only approximate for mixtures of lævulose and sucrose, in which case the angular rotation is a little smaller (or larger numerically if negative) than that calculated. The polariscopic determination of the percentage of sucrose replaced by invert-sugar gives slightly high results; this applies whether the source of light in the measurements is that of the sodium flame or a suitably purified mercury flame. In the latter case the error

is not so large as in the former case. The presence of a constant amount of hydrochloric acid at a concentration, 0·1N, sodium chloride 0·1N, or sodium carbonate 0·04N has no effect on the percentage determinations of sucrose when the rotations of the pure sucrose and invert-sugar are determined under the same conditions as in the case of the mixtures. The error introduced by the polariscopic method of analysis is small enough to be neglected in most sucrose hydrolysis investigations, both in hydrolysis by acids and hydrolysis by invertase when properly carried out in the latter case. It is such as to cause neither increasing nor decreasing velocity coefficients, but would cause the coefficients to be too high by about 4 parts in a thousand when sodium light is used, and quite appreciably less in error if mercury-vapour light is used in the polariscopic measurements. J. F. S.

Relation of Molecules to Slow Free Electrons. H. F. MAYER (*Ann. Physik*, 1921, [iv], **64**, 451—480).—The absorption of very slow cathode rays in hydrogen, nitrogen, carbon dioxide, helium, and argon was investigated. With velocities below 8 volts the absorbing cross-section of the molecules remained constant except in the case of argon, in which case the specific capacity of absorption increased to a maximum with diminishing speed to 12 volts and then diminished to a very small value. Argon possesses a pronounced selective absorption; the other gases show no selective absorption. J. R. P.

Spectrum-analytical Investigations of the Canal and Cathode Rays of the Positive Point Discharge in Oxygen and Nitrogen. ALBERT SCHULTZ (*Ann. Physik*, 1921, [iv], **64**, 367—375).—In the spectrum of the positive point current in oxygen the spark lines, series lines, doublet lines of the second arc spectrum, the first band spectrum and ozone bands were observed. In nitrogen, positive bands, negative bands, and spark lines were found. In the positive point current, slow cathode rays, rapid cathode rays and slow canal rays, corresponding with two regions of ionisation, occur. The distribution of intensity of the lines may be explained on the following assumptions. The carrier of the series lines of oxygen is the univalent atom-ion; that of the spark lines is the bivalent atom-ion. The carrier of the negative bands in nitrogen is the bivalent diatomic molecule-ion, N_2^{++}, that of the positive bands the univalent diatomic molecule-ion N_2^{+}. In the canal rays of the positive point current changes of charge occur; in nitrogen from bivalent to univalent molecule-ions and in oxygen from bivalent to univalent atom-ions. J. R. P.

Röntgenograms obtained by Means of Mica Piles composed of Crossed Lamellæ. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 676—678).—Further experiments have shown that the conclusion reached in a former paper (A., 1920, ii, 601) that the Röntgen ray images obtained from a system of mica lamellæ crossing at definite angles were not mere super-

positions of the images obtained from each of the composing lamellæ separately, cannot be maintained. E. H. R.

Radioactive Constants according to the Position in 1920. STEFAN MEYER (*Jahrb. Radioaktiv Elektronik*, 1920, **17**, 80—87).—Tables of constants deduced from the most trustworthy data are given for the various families of radioactive elements. The tables include the half life, disintegration constant, the average life, the initial velocity of the corpuscles, the absorption coefficient for aluminium and lead, and the range of the particles. J. F. S.

Power of Emission of the Metals and Methods for its Determination. F. HENNING (*Jahrb. Radioaktiv Elektronik*, 1920, **17**, 30—62).—A theoretical discussion on the emissivity of metals in which it is shown from the investigations of Hagen and Rubens (A., 1909, ii, 358; 1910, ii, 262, 469), that the formulæ $A = 1 - R = 0{\cdot}365\ (\gamma/\lambda)^{1/2} - 0{\cdot}0667\ \gamma/\lambda + 0{\cdot}0091)\ (\gamma/\lambda)^{3/2} - \ldots$ and $A = 0{\cdot}365\ \sqrt{\gamma/\lambda}$ in which A is the power of absorption and R the reflection, represent the absorptive power of the metals for long wave-lengths (26μ). At the wave-length $\lambda = 8{\cdot}85\mu$ marked deviations from the theory are already observed, which, however, only show themselves in the absolute quantity and do not appear in the temperature coefficient of the absorptive power. The temperature coefficient is still in fair agreement with theory for wave-lengths 4—5μ, but on passing to still shorter wave-lengths it suddenly deviates from the theoretical value, and at 2μ the absorptive power of the metals is independent of the temperature, whilst at longer wave-lengths it has a positive temperature coefficient. The absorptive power of tantalum and the platinum metals in the visible spectrum is constant. In the case of tungsten, experimental results of various observers are at variance; some regard it as constant whilst others assign a negative or a positive temperature coefficient to it. The radiation properties of tungsten are very much influenced by impurities, and this probably accounts for the above-mentioned diversity in the results. Many observers have found that molten gold, silver, copper, nickel, palladium, and platinum have a stronger power of emission in red light and a weaker power of emission in blue light than the solid metals, whilst in the case of molten tungsten Langmuir (*Phys. Rev.*, 1915, **6**, 138) has found that it radiates weaker in red light than the solid metal, whilst Bidwell (*Phys. Rev.*, 1914, **3**, 439) only found a difference when oxygen was present. In calculating the intensity of radiation in the visible region the following values of the power of emission are recommended where the λ values are given in 0·001 mm.

λ.	Ag.	Au.	Pd.	Pt.	Rh.	Ir.	Ta.	W.
0·45	0·10	0·67	—	0·45	—	—	—	0·52
0·50	0·09	0·53	—	0·42	0·24	0·28	0·62	0·51
0·55	0·07	0·26	—	0·39	0·23	0·27	0·60	0·50
0·60	0·07	0·16	0·33	0·36	0·22	0·25	0·58	0·49
0·65	0·06	0·11	—	0·33	0·21	0·24	0·56	0·47
0·70	0·05	0·08	—	0·31	0·20	—	—	0·46

J. F. S.

Work of Ionisation and Dissociation of Hydrogen. THEA KRÜGER (*Ann. Physik*, 1921, [iv], **64**, 288—304).—The first strong ionisation of hydrogen occurs at 17·1 ± 0·25 volt, the second at 30·4 ± 0·5 volt. The first value is attributed to the dissociation of the molecule and the ionisation of one atom; the second value is supposed to correspond with the dissociation of the molecule and the ionisation of both atoms. The work of dissociation of the molecule is thus calculated as 3·5 ± 0·3 volt, or 81300 ± 5700 gram cal.

At 11 volts weak ionisation, and at 13·5 volts radiation occur. The radiation at 13·5 volts is attributed to dissociation of the molecule with simultaneous resonance radiation of one atom; the value 11 volts is assumed provisionally as the energy of formation of a hydrogen molecule. J. R. P.

The Electrical Resistance of Nickel Steels. A. PORTEVIN (*Compt. rend.*, 1921, **172**, 445—447).—The electrical resistance of nickel steels depends to a considerable extent on the conditions of annealing. Differences of 10—40% in the value were obtained with steels containing 0·3—0·8% of carbon and 7—15% of nickel, according as the samples were heated to 1000° and cooled during 4—5 hours or heated to 1300° and cooled during three days. This variation in the electrical resistance may or may not be accompanied by characteristic modifications of the micro-structure. Curves are given showing the variation in resistance of nickel steels according to their carbon and nickel content. W. G.

Zinc Electrode. WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1921, **43**, 81—84).—Reproducible and trustworthy measurements of the potential difference of zinc electrodes can only be obtained when the solutions are made with freshly boiled water from which all oxygen is excluded by a constant stream of hydrogen. Even this arrangement does not indicate small changes in the zinc ion concentration, and it is suggested that substituting a dilute zinc amalgam for the zinc rod will probably give satisfactory results in these cases. J. F. S.

The Mobility of Univalent Organic Ions. G. VON HEVESY (*Zeitsch. Elektrochem.*, 1921, **27**, 77—78).—A reply to Lorenz's criticisms (A., 1919, ii, 212). The contradiction between the author's results and those of Lorenz is only apparent. Most univalent organic ions are already so large, and consequently the strength of their electrical field is so small, that they do not become hydrated. Lorenz's objections to the author's views would only hold (*a*) if univalent organic ions were known with mobilities greater than 60, and (*b*) if ions exceeding the "normal" size became hydrated. E. H. R.

Depolarisation by Light. EMIL BAUR (*Zeitsch. Elektrochem.*, 1921, **27**, 72—77).—From the work of Staechlin on the effect of fluorescent dyes on the *E.M.F.* of illuminated cells (A., 1920, ii, 580), it was to be expected that a light-sensitive substance in an

electrolytic cell would have a depolarising action in the light. Experiments were made to test this conclusion by comparing the current-tension curves of such cells in the light and dark respectively. The cells used contained dilute sulphuric acid solutions of uranyl sulphate or quinine sulphate, or a dilute sodium carbonate solution of eosin. The electrodes were of platinum and the cells were so arranged that the anode or cathode separately or both together could be illuminated by means of a 3000 candle-power half watt lamp. A variable *E.M.F.* was applied to the cell and the current–*E.M.F.* curve was plotted, or alternatively, with a constant *E.M.F.*, the current–time curve was plotted for the illuminated and un-illuminated cell. In each case the depolarising effect of the light-sensitive substance was clearly shown in the illuminated cell. In the case of uranyl sulphate the cathode effect (with only the cathode illuminated) was much smaller than the anode effect, whilst with quinine sulphate and eosin this difference did not appear in the current–*E.M.F.* curves, although it was clearly marked in the current–time curves with constant *E.M.F.* By rotating or shaking the cell it was possible to get a higher current with a given *E.M.F.* in either the illuminated or unilluminated cell, but in each case the illuminated cell gave a much higher current. A shaken, illuminated cell gave for 20 hours a constant current actually higher than the initial current of the same cell in the dark. It must be concluded that polarisation has an immediate effect on the current strength in the dark. The experiments show that the depolarising effect of light is in agreement with the hypothesis of a concealed water-photolysis (Staechlin, *loc. cit.*). E. H. R.

The Magnetisability of the Rare Earths. E. WEDEKIND [with P. HAUSKNECHT] (*Ber.*, 1921, **54**, [*B*], 253—258. Compare A., 1915, ii, 140).—The following values have been obtained for the atomic magnetism, $\gamma\alpha \times 10^{-6}$, of a series of metals of the rare earths, the observations being made with spectroscopically pure specimens of the oxides, sulphate, and oxalates :

	Sc.	Y.	La.	Ce^{iii}.	Ce^{iv}.	Pr.	Nd.	Sm.	Gd.	Er.
Oxide	−1·2	+8·7	−18·3	—	+74·4	+4740	+5100	+8300	+9850	+40,600
Sulphate	−62·5	−57	−84	+2200	+37·5	+5100	+5270	—	—	+36,700
Oxalate	−65	—	—	—	—	+5000	+5380	—	+9430	+35,800

The values for scandium, yttrium, and lanthanum are too small to be regarded as trustworthy.

If the values for the atomic magnetism are plotted against atomic weights a graph is obtained which shows a flat maximum at yttrium, and a second maximum in the cerite group, either at neodymium or samarium, according to the value adopted; the curve then descends to europium and subsequently rises somewhat steeply but regularly through gadolinum and terbium to a high maximum at dysprosium, after which it falls steeply and evenly through holmium, erbium, ytterbium, to lutetium.

H. W.

Specific Heats of some Organic Liquids. ROBERT TRÉHIN (*Ann. Physique*, 1921, [ix], **15**, 246—263).—The liquid was heated

electrically in a Dewar vessel and the energy supplied measured. The rise in temperature was measured by a mercury thermometer. The Dewar vessel was immersed in a water-bath which was kept at the same temperature and the corrections for radiation thus eliminated. The results found, with an accuracy of 1 in 200, were: benzene $c = 0{\cdot}405 + 93 \times 10^{-5} (t - 15)$; toluene $c = 0{\cdot}410 + 107 \times 10^{-5} (t - 15)$; acetone $c = 0{\cdot}510 + 80 \times 10^{-5} (t - 15)$; chloroform $c = 0{\cdot}226 + 33 \times 10^{-5} (t - 15)$. In all cases c is the true specific heat; t the temperature. The effects of impurities are discussed.
J. R. P.

Molecular Heat of Hydrogen. F. H. MacDougall (*J. Amer. Chem. Soc.*, 1921, **43**, 23—28).—On the basis of Bohr's views with regard to the constitution of the hydrogen molecule, and on the assumption that the rotational energy corresponds with three degrees of freedom, the author has deduced formulæ by which the molecular heat of hydrogen may be calculated from the absolute zero up to 2600° abs. The results calculated by means of these formulæ are compared with the values put forward by Nernst (*Physikal. Zeitsch.*, 1912, **13**, 1064) and Pier (A., 1909, ii, 789; 1910, ii, 1031).
J. F. S.

Critical Temperature of Mercury. G. Meyer (*Physikal. Zeitsch.*, 1921, **33**, 76—78.)—The critical temperature of mercury has been calculated from measurements of the surface tension of mercury at 20° and 367° (Hagemann, *Diss. Freiburg i Br.*, 1914). From the measurements it is shown that the surface tension (α) against mercury vapour is represented by the formula $\alpha = 474{\cdot}7 - 0{\cdot}148t - 0{\cdot}000344t^2$ dyne/cm². Using this formula, the values of α, $\alpha(M/\rho)^{2/3}$, the molecular surface energy and $d/dt(\alpha[M/\rho]^{2/3})$ the temperature coefficient are calculated for every 20° from 20—360°. The number of double molecules is obtained, and it is shown that at 340° the value of the temperature coefficient is normal. Hence using the formula $d/dt(\alpha[yM/\rho]^{2/3} = -2{\cdot}121$, it follows that $\alpha(yM/\rho)^{2/3} = C - 2{\cdot}121t$ and for $t = 340°$ $y = 1$. Hence $C = 3125$. At the critical temperature $\alpha = 0$, hence $C = 2{\cdot}121t_k$ or $t_k = 1474°$. This value is compared with other values, with some of which it is in close agreement.
J. F. S.

Melting Point Apparatus. Fritz Friedrichs (*Zeit. angew. Chem.*, 1921, **34**, 61).—In a melting-point apparatus, the glass heating bath, surrounding the thermometer, is of oval section with flattened front and back, so that readings may be made microscopically without interference due to the curvature of the glass. The thermometer and melting-point tubes are, in addition, enclosed in an inner vessel of similar cross-section, which serves to overcome the thermometer lag; and for conveniently assembling the apparatus without removing the thermometer, the outer vessel is provided with oblique lateral tubular extensions through which, and through orifices in the inner vessel, the melting-point tubes are introduced near to the thermometer bulb.
W. J. W.

Piezoelectric Analysis. II. Investigation of Systems of which the Temperature of Solidification can pass through a Maximum. JEAN TIMMERMANS (*Bull. Acad. Roy. Belg.*, 1919, 753—766; from *Chem. Zentr.*, 1921, ii, 281. Compare A., 1914, ii, 109).—The author discusses the form of the piezometric curves for a pure substance the freezing point of which passes through a maximum with increasing pressure. Similar considerations are applied to mixtures of substances of this type. H. W.

Piezochemical Analysis. III. Crystallisation under Increased Pressure and its Relationship to the Mutual Solubility of Liquids. JEAN TIMMERMANS (*Bull. Acad. Roy. Belg.*, 1919, 767—785; from *Chem. Zentr.*, 1921, ii, 281. Compare preceding abstract).—The process of solidification of systems consisting of two liquid layers under high pressure is investigated theoretically and illustrated by many piezochemical curves. The original must be consulted for details. H. W.

The Lowering of the Vapour Pressure of Water at 20° Produced by Dissolved Potassium Chloride. B. F. LOVELACE, J. C. W. FRAZER, and V. B. SEASE (*J. Amer. Chem. Soc.*, 1920, **43**, 102—110).—The vapour pressure of solutions of potassium chloride of concentrations from 0·05N to 4·0N has been determined by the Frazer and Lovelace static method (A., 1915, ii, 11). The lowering of the vapour pressure and the molecular lowering are calculated and curves are constructed. The molecular lowering curve is found to be irregular at 20° and passes through a distinct minimum at the concentration N. The vapour pressures of potassium chloride solutions were calculated from freezing-point data by means of von Babo's law and an equation connecting freezing-point lowering with vapour pressure. The calculated values varied from about 3% greater than the observed values in the dilute solutions to about 6% less in the concentrated solutions. The percentage ionisation of dilute solutions of potassium chloride was calculated by comparing the vapour pressure lowerings with the lowerings produced by mannitol, and the values obtained agreed well with the best values from freezing point and conductivity data. J. F. S.

Vapour Pressures and the Isothermals of Vapours. J. H. SHAXBY (*Phil. Mag.*, 1921, [vi], **41**, 441—454).—Consideration of the internal pressure in fluids leads to the relation that in "ideal" substances the ratio of the occupied volume (covolume) to the total volume of the liquid is equal to the ratio of the unoccupied volume to the total volume of its saturated vapour. The two phases, in equilibrium with each other, are complementary in this respect. The equation $p = RT(d_1 + d_2)(d_2/d_1)^{(d_1+d_2)/(d_1-d_2)}$ is obtained for the saturation pressure of a vapour in terms of the temperature and the densities of the two phases at that temperature. This leads to a characteristic equation—

$$p[v - 1/(d_1 + d_2)] = RT(d_2/d_1)^{2/(d_1-d_2)v}.$$

It is shown that the quantity $d_1 + d_2$ may be regarded as a density factor which is a measure of the cohesive forces per unit mass. On this hypothesis modified forms of the above equations are obtained which express the experimental facts with considerable accuracy for all temperatures and pressures. Reduced forms of the vapour pressure equation are given as well as an equation for the calculation of the critical density of a substance. The values are consistent even with water, where the Mathias rule does not hold. J. R. P.

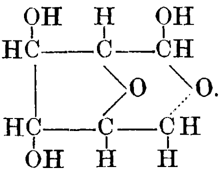
The Mechanism of the Exchanges of Energy in Vaporisation. RENÉ AUDUBERT (*Compt. rend.*, 1921, **172**, 375—378).—The author deduces the equation $MJL = \alpha\pi d^2N + RT$, where M is the molecular weight, J the mechanical equivalent of the calorie, L the latent heat of vaporisation, α the surface tension of the liquid, d the diameter of a molecule, and N Avogadro's number. From this he calculates for a number of liquids the value of d at two temperatures. The results agree with those obtained from the kinetic theory or from Bragg's work. Combining the above with Clapeyron's formula, an expression is obtained for the variation of vapour pressure with temperature, which is of the form obtained by Dupré and others. It is further shown that vaporisation is a discontinuous phenomenon, the elementary quantity of energy brought into action being $10 \times 10^{-16}\ T_0$ ergs. Finally, the value obtained for K in $\alpha\pi Nd^2 = K(T_c - T)$ is practically identical with that deduced from the law of Eötvös. W. G.

Determination of the Boiling Point of very Small Quantities of Substances. VICTOR ARREGUINE (*Ann. Chim. anal.*, 1921, [ii], **3**, 40—49).—The method proposed depends on the pressure of vaporisation and is similar to that described previously by Schleiermacher (A., 1891, 873). W. P. S.

Cottrell's Ebullioscopic Apparatus. JAMES FREDERICK SPENCER (*J. Amer. Chem. Soc.*, 1921, **43**, 301—302).—Modifications of the ebullioscopic apparatus described by Cotterell (A., 1919, ii, 447) and Read and Washburn (A., 1919, ii, 447) are suggested. These consist in replacing the two-limbed pump by a three-limbed pump, which will ensure a more uniform spraying of the thermometer bulb, and making both pump and condenser separate from the rest of the apparatus, which makes the apparatus less fragile and easier to clean. J. F. S.

The Chemical Constants. G. HEIDHAUSEN (*Zeitsch. Elektrochem.*, 1921, **27**, 69—72).—A theoretical paper in which the values of the chemical constants are calculated from Egerton's determinations of the vapour pressure of zinc and cadmium. The values calculated from Nernst's formula are, for zinc, — 1·62 and for cadmium, — 1·56. These results differ to some extent from those obtained by Egerton (A., 1920, ii, 84), but agree with the value, 1·59, calculated from the Sackur-Stern-Tetrode formula. E. H. R.

Calculation of the Heating Value from the Constitution of the Compound. F. OTTO H. BINDER (*Chem. Zeit.*, 1921, **45**, 141).—A method of calculating the heating value of a substance from its constitutional formula is given and illustrated in the case of cellulose, which is given the annexed constitutional formula.



Here 3 oxygen valencies are bound to hydrogen, and 6 oxygen valencies are bound to carbon, and a seventh oxygen valency, represented by the dotted line, may be regarded as bound to carbon. These valencies do not contribute to the heat effect on combustion. The calculation is effected thus: O_2 when it burns to carbon dioxide gives 96,960 cal., that is, 48,480 cal. per atom and 24,240 per valency, O_2 when it burns to water gives 68,920 cal. or 34,460 per valency. Cellulose contains 6 carbon atoms, which, on burning to carbon dioxide, give $6 \times 96{,}960 = 581{,}760$ cal., and the 10 hydrogen atoms give 344,600 cal., that is a total of 926,360, but from this $3 \times 34{,}460$ and $6 \times 24{,}240 = 145{,}440$ cal. must be subtracted, since this represents the heat effect of the valencies already bound. The total is therefore 677,540 cal. per gram-mol. or 4,182 cal. per gram, whilst the observed value is 4,189 cal. per gram. J. F. S.

Thermodynamic Treatment of Concentrated Solutions and Applications to Thallium Amalgams. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1921, **43**, 233—254).—A number of methods are developed for the thermodynamical treatment of concentrated solutions, and for the rapid and precise calculation of partial molecular quantities; these methods are applied to the data for thallium amalgams (Richards and Daniels, A., 1920, ii, 34, and Hildebrand and Eastman, A., 1916, ii, 14). It is shown how the heat of solution of solid thallium and supercooled liquid thallium in a large excess of mercury may be obtained, and how these quantities may be used for calculating the heat of fusion of thallium. The activities of thallium and mercury in amalgams of various compositions are given for 20° and 325°, and these values, resting on independent measurements, are compared by simple thermodynamic methods. The effect of temperature on the abnormality of solutions is discussed, and it is shown that the vapour pressure of amalgams at 325° may be calculated by two methods from the measurement of *E.M.F.* at 20°, between which two results the true value must lie. Thus in 40% amalgam the vapour pressure was found by one method to be 1% higher and by the other to be 2% lower than the calculated value. J. F. S.

Viscosity of Liquids. V. The Ideality of the System: Benzene–Benzyl Benzoate and the Validity of the Bingham Fluidity Formula. JAMES KENDALL and KENNETH POTTER MONROE (*J. Amer. Chem. Soc.*, 1921, **43**, 115—125. Compare

A., 1920, ii, 670).—It has been claimed by Bingham and Sarver (A., 1920, ii, 737) that the system, benzene–benzyl benzoate is not ideal (perceptible contraction, presumably owing to solvation, occurring on mixing), and that consequently the conclusions of Kendall and Monroe (A., 1917, ii, 524) from their examination of the system are not valid, particularly their rejection of the fluidity–volume composition formula as the true ideal equation for binary liquid mixtures. An examination of Bingham and Sarver's experimental data, which are necessarily somewhat inaccurate owing to the impurity of the benzyl benzoate employed, shows that the contraction claimed is non-existent. Freezing point depression determinations also indicate the absence of compound formation. The system is, as previously asserted, essentially ideal. A critical investigation of the experimental and theoretical evidence for the validity of the linear fluidity–volume composition formula for ideal mixtures has not, in the author's opinion, disclosed any facts which warrant its reconsideration. The formula is systematically in error; other equations are known which are in far better agreement with fact, but the true ideal equation still remains to be discovered.

J. F. S.

Orientation of Molecules in Surfaces. VI. Cohesion, Adhesion, Tensile Strength, Tensile Energy, Negative Surface Energy, Interfacial Tension, and Molecular Attraction. WILLIAM D. HARKINS and Y. C. CHENG (*J. Amer. Chem. Soc.*, 1921, 35—53. Compare A., 1920, ii, 357).—Data are obtained whereby the total interfacial energy may be calculated for twelve organic liquids, and the work of adhesion and of surface cohesion, the interfacial tension and free surface energy, the tensile work, the energy of adhesion, of cohesion, and of surface cohesion, the tensile energy, the internal pressure or cohesion, and the related molecular attraction are discussed. The present data include two new and important relations, (i) that certain surface or interfaces between two liquids exhibit a negative surface energy, or, in other words, energy is set free when the surface is formed. This is just the opposite of previous results for all surfaces previously known, with the exception of the case when crystalline liquids are undergoing transformation, have required the expenditure of energy for their formation; (ii) whilst ordinary surfaces cool when they are expanded, these surfaces, and some others discovered in the present investigation, rise in temperature when they are formed. The liquids at the phase boundary of which with water a negative surface energy is exhibited are heptinene (with a triple bond at the end of the chain), *n* and *sec.*-octyl alcohol, and heptaldehyde. All the above liquids and a higher paraffin have a negative latent heat of the phase boundary, which indicates that the interface rises in temperature when it is expanded. The addition of one oxygen-atom to octane to give octyl alcohol increases the tensile energy by only 2%, whilst it increases the adhesional energy by 65%, and similar relations are found for the organic acids, aldehydes, and heptinene. In contrast with this, it is found that the double bonds increase the tensile

energy greatly, about 40%, in the change from hexane to benzene, whilst the adhesional energy towards water is increased only 30%. It is found also that the very symmetrical halogen derivatives, carbon tetrachloride, and ethylene dibromide, which give especially high values for their own tensile energy, give especially low values for their adhesional energy toward water. The tensile energy of ethylene dibromide, on account of its symmetry, is higher than that of ethylidene bromide. These facts are readily explained on the basis of the hypothesis that the unsymmetrical molecules are oriented in the surface, and therefore afford strong evidence in favour of the orientation hypothesis. When a bar of heptinene (or of an organic acid, alcohol, aldehyde or amine) is pulled apart, the break occurs where the electromagnetic field (largely electrical) and the resulting attraction are weakest, that is, between the hydrocarbon chains, and in order that this may be the case the hydrocarbon chains turn into the nascent surface in the process of its formation. In benzene, the symmetry of the molecules is so great that the break must occur between certain of the unsaturated groups, that is, where the intramolecular electromagnetic field is high. The fact that the adhesional energy of octane is so greatly increased by the addition of one oxygen atom to form octyl alcohol indicates that the oxygen atoms turn towards the water at their interface. Thus the adhesional energy toward water is determined by the strongest electro-magnetic fields in the molecule, while the tensile energy is determined by the weakest fields, provided the molecules are unsymmetrical. The solubilities of heptoic acid, heptinene, and heptaldehyde have been determined and are found to be nearly the same, which indicates that the length of the hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule, provided that the activity of the latter is not too widely varied. The triple bond in heptinene is found to increase the adhesional work from about 42 to 67, and the total adhesional energy from 105 to 147, the lower values being those for hexane. The introduction of one oxygen atom increases the adhesional work to 90, and the energy to 164. This indicates that the triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with an hydroxyl oxygen atom. J. F. S.

Colour and Brownian Movement of Ultra-microscopic Metallic Particles. Reinhold Fürth (*Physikal. Zeitsch.*, 1921, **33**, 80—87).—The colour and Brownian movement of gold and silver particles have been observed in a large number of cases in an ultra-microscope. From the observations the radii of the particles were calculated (i) by means of the Helmholtz theory, and (ii) by means of Einstein's theory. It is shown that between both series of results there is no systematic variation in the sense of $a_{Br} > a_F$ for gold or $a_{Br} < a_F$ for silver, where a_{Br} is the radius obtained from the Brownian movement and a_F that from the colour. J. F. S.

Augmented Adsorption. G. WIEGNER, J. MAGASANIK, and A. J. VIRTANEN (*Kolloid Zeitsch.*, 1921, **28**, 51—76).—The adsorption of a series of saturated aliphatic acids from water and also from solutions of various concentrations of sodium chloride, potassium chloride, lithium chloride, ammonium chloride, calcium chloride, magnesium chloride, barium chloride, strontium chloride, and sodium sulphate by blood charcoal has been determined. The surface tension of all the solutions used for adsorption experiments was determined at ordinary temperatures. It is shown that the adsorption equilibrium between the fatty acids in aqueous solution and blood charcoal is displaced by the presence of neutral salts in the sense that more of the fatty acid is adsorbed than in pure aqueous solution. Double normal solutions of the salts mentioned above increase the amount of fatty acid adsorbed by blood charcoal. The augmentation of the adsorption of the fatty acids increases with decrease of the atomic weight of the kation for equivalent kations. The sulphanion augments the adsorption more than the chlorion at ordinary temperatures, but at the boiling point the relationship is reversed. The lowering of the surface tension of salt solutions of fatty acids compared with salt solutions is greater than that of fatty acid solutions compared with water. The lowering of the surface tension of the solution examined runs parallel with the amount of fatty acid adsorbed by charcoal. It is shown that the adsorption of fatty acids from aqueous solutions or from salt solutions by charcoal may be approximately calculated from the surface tension of these solutions. All the salts examined have a greater effect on the adsorption the greater the number of carbon atoms in the acid under investigation. The relationship between the concentration of the fatty acid in solution and that adsorbed by the charcoal is expressed by the formula $x/m = kc^{1/n}$, in which x/m represents the number of millimols. of acid adsorbed by 1 gram of charcoal, c is the equilibrium concentration of the acid in solution, and k and n are empirical constants. The lowering of the surface tension follows a similar exponential formula. With a constant salt concentration the value of k is greater than for pure aqueous solutions, the value of $1/n$ is also a little larger with salt solutions. The adsorption curves for low concentrations of fatty acids, both with and without addition of salts, are therefore approximately the same, but with increasing concentration of the fatty acids and with constant salt concentration the adsorption is increasingly augmented. The surface tension changes in the same sense. Addition of salt to a constant concentration of fatty acid increases the adsorption proportionally with the salt concentration. The increase of the surface tension of the neutral salt is, within defined concentrations, approximately proportional to the concentration of the salt, so that the lowering of the surface tension of a fatty acid of constant concentration as solvent by the addition of salt is increased by an amount proportional to the salt concentration. It is shown experimentally for the case fatty acid–salt solution that an augmentation of the adsorption can occur when one substance increases the surface tension, solution–

air, whilst the other lowers it. The adsorption augmentation of acetone, ethyl alcohol, and dextrose in aqueous solution by the presence of 2*N*-sodium chloride has also been investigated.

J. F. S.

Comparative Experiments on the Adsorptive Capacity of Various Kinds of Charcoal. Is Wiechowski's Test Parallel to the Poison Fixation? FRIEDRICH HORST (*Biochem. Zeitsch.*, 1921, **113**, 99—110).—Wiechowski's and Joachimoglu's methods (A., 1917, ii, 42) for the determination of the adsorptive capacity of charcoal is applicable to chemically defined poisons but not to toxins such as diphtheria, tetanus, and ricin toxins.

S. S. Z.

Study of Crystals by *X*-rays. FRANÇOIS CANAC (*Ann. Physique*, 1921, [ix], **15**, 153—246).—An account of the theory of the determination of crystal symmetry by the *X*-ray method. An apparatus for carrying out the determinations is described.

J. R. P.

Determination of the Structure of Crystals. RALPH W. G. WYCKOFF (*J. Franklin Inst.*, 1921, **191**, 199—230).—A brief survey of the work done on the structure of crystals by the *X*-ray method, with a discussion of some of the limitations of the latter.

J. R. P.

Application of the Theory of Space Groups to the Study of the Structure of Crystals. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1921, [v], **1**, 127—137).—The paper is an attempt to present those details of the theory of space groups which are required in order that the results of the theory may be immediately applicable to the determination of the structure of crystals. The 230 possible space groups are obtained by arranging the 32 possible point groups in a regular pattern corresponding with one or other of the fourteen space lattices, of the same symmetry as the point group. The space grouping thus obtained can be divided into units of structure corresponding with the "crystal molecule," the dimensions of which are revealed by *X*-ray examination of a crystal. The *X*-ray spectrum measurements also indicate the number of chemical molecules contained in the crystal molecule. With the limitations imposed by the results thus obtained, the theory of space groups can be applied to determine the probable positions of the atom in the crystal molecule.

E. H. R.

Liquid Crystals. V. Photographic Absorption and Extinction Measurements. (MISS) RASSA RIWLIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 807—816. Compare A., 1919, ii, 101).—A photographic method is described for measuring the light absorption of any substance. The method was applied to *p*-azoxyanisole, and it was shown that in the visible spectrum, as in the infra-red region, the two liquid-crystalline phases, ex-solid and ex-liquid, have different absorptive powers.

E. H. R.

The Thermo-Electric Determination of Transition Points. A. SMITS and J. SPUYMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 687—690).—When the *E.M.F.* of a thermocouple is plotted against temperature a smooth curve is generally obtained, but if one of the metals has a transition point within the temperature range considered, a discontinuity appears at the corresponding temperature. This phenomenon has been found to afford a rapid and accurate method for determining the transition temperature of tin. Using an iron–tin thermo-element, the transition temperature found was 200·2°. This agrees perfectly with the result obtained by the laborious dilatometric method, using mercury to accelerate the transformation of the tin. With a copper–tin thermo-element, very nearly the same result was obtained, 200·5°, but the break in the curve was not so sharp as with the iron–tin combination.

E. H. R.

The General Structure of Colloids. WOLFGANG PAULI (*Kolloid Zeitsch.*, 1921, **28**, 49—51).—A consideration of the physical-chemical analysis of ferric hydroxide sols shows that this substance is a complex salt of the type $x\,\mathrm{Fe(OH)_3}\,y\,\mathrm{Fe}/An$, where An is the anion in the presence of which the sol is formed. In the case of zirconyl chloride the following complex molecules have been identified: $\mathrm{Zr(OH)_4,Zr(OH)_4,ZrOCl_2,\overset{++}{ZrO} \mid \overset{--}{Cl_2}}$;

$$\mathrm{Zr(OH)_4,ZrOCl_2,\overset{--}{ZrO} \mid \overset{++}{Cl_2}};$$

$\mathrm{Zr(OH)_4,\overset{++}{ZrO} \mid \overset{--}{Cl_2}}$ and $\mathrm{ZrOH_4,Zr(OH)_2Cl_2,\overset{--}{Cl_2} \mid \overset{++}{H_2}}$. Similarly, molecules are found in the case of aluminium hydroxide sols. The question of the structure of metallic sols, such as gold sols, is considered, and it is shown here, also, that these sols are not composed of extremely small particles of the metals, but are complexes of the same type as those mentioned above.

J. F. S.

The Validity of the Law of Partition for the Equilibrium between a Mixed Crystal Phase and a Coexisting Liquid. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 679—686).—Experiments were made to determine the distribution of dichlorobenzene and dibromobenzene (? para) in the system, dichlorobenzene–dibromobenzene–alcohol in the mixed crystal and liquid phases. On both the dichloro- and dibromo-benzene sides the partition law was found to hold when the concentration of one constituent was relatively small in comparison with that of the other, that is to say, the ratio of the concentrations in the liquid and solid phases respectively was constant. E. H. R.

Equilibrium Conditions of the Reaction between Manganate, Permanganate, and Manganese Dioxide. CHARLES E. RUBY (*J. Amer. Chem. Soc.*, 1921, **43**, 294—301).—The composition of equilibrium mixtures of potassium manganate and permanganate and the equilibrium constants have been determined at 45°; the equilibrium constant is given by the expression

$[MnO_4']^2[OH']^4/[MnO_4'']^3$ and has the value 53. The decrease in free energy accompanying the reaction $3K_2MnO_4 + 2H_2O = MnO_2(s) + 2KMnO_4 + 4KOH$, assuming that all the substances are completely ionised, is 10,500 joules and the *E.M.F.* of a cell in which it takes place is $+0.054$ volt. Regarding this *E.M.F.* as having the same value at 25° and combining it with the normal electrode potential (-0.61 volt) of $MnO_4'' + \oplus = MnO_4'$ (Sackur and Tagener, *Zeitsch. Elektrochem.*, 1915, **18**, 718), the following molecular electrode potentials are derived: $MnO_2(s) + 4OH' + 2\oplus = MnO_4'' + 2H_2O$, -0.664 volt; $MnO_2(s) + 4OH' + 3\oplus = MnO_4' + 2H_2O$, -0.647 volt; and $MnO_2(s) + 2H_2O + 3\oplus = MnO_4' + 4H^{\cdot}$, -1.757 volts. J. F. S.

The Equilibrium, Gelatin-Hydrochloric Acid. ROBERT WINTGEN and KARL KRÜGER (*Kolloid Zeitsch.*, 1921, **28**, 81—89).—The velocity of hydrolysis of methyl acetate by $0.05N$ and $0.10N$ hydrochloric acid in the presence of varying amounts of gelatin has been determined at 25°. The reaction mixtures were prepared as follows: 0, 0·1, 0·2, 0·5, 1·0, 2·0, 3·0, 4·0, and 5·0 grams of air-dried gelatin were placed respectively in a series of 100 c.c. flasks and dissolved at 70° in about 30 c.c. of water. After cooling to 25° in a thermostat, 50 c.c. of $0.1N$ or $0.2N$ hydrochloric acid were added, followed by 5 c.c. of methyl acetate, and the volume was made up to 100 c.c. The solution was titrated at periods up to 7,417 minutes. It is shown that the velocity constant decreases steadily with increasing gelatin content; thus for $0.05N$-hydrochloric acid the velocity constant R falls from 1.446×10^{-4} in the absence of gelatin to 0.052×10^{-4} for a content of 6 grams of gelatin per 100 c.c. With $0.1N$-hydrochloric acid the value of R falls from 2.850×10^{-4} in the absence of gelatin to 1.589×10^{-4} for a content of 5 grams of gelatin per 100 c.c. Making use of a slightly modified formula due to Sörensen (A., 1919, i, 175, 176, 177), the value of R is calculated on the assumption that one amino-group of the gelatin reacts with hydrochloric acid according to the equation $[Ge]NH_2 + HCl = [Ge]NH_3Cl$, so that in aqueous solution the equilibrium $[Ge]NH_3Cl + H_2O \rightleftarrows [Ge]NH_3{\cdot}OH + HCl$ is established, and it is found that the experimental values are always a little greater than the calculated values. The hydrogen-ion concentration has also been determined and calculated, and here a satisfactory agreement is obtained. The molecular weight of gelatin is deduced from the experimental data as 1,014 and K, the hydrolysis constant of the gelatin hydrochloride, as 4.139×10^{-4}, and from this the basic hydrolysis constant $k_b = k_w/K = 2.7 \times 10^{-11}$, where k_w is the ionic product of water. J. F. S.

The Displacement of Metals in Saline Solutions. BARLOT (*Compt. rend.*, 1921, **172**, 378—381).—The precipitation of one metal from a solution of one of its salts by another more electronegative metal, such as the precipitation of copper by zinc, may most readily be followed by soaking a piece of filter paper in a solution of a copper salt, placing it on a glass plate, and then placing a

fragment of zinc on the paper. It is shown that the copper crystallises out radially from the zinc, the lines of crystals not crossing. If two or more fragments of zinc, not touching, are used, there is apparently a neutral zone between the fragments, which the copper crystals do not cross.

W. G.

The Double Saline Decompositions and their Geometric Representation. HENRY LE CHATELIER (*Compt. rend.*, 1921, **172**, 345—350).—A diagram is figured and described by means of which it is possible to solve the following problems: (1) the determination of the mixtures of three salts having a composition identical with that of the mixture considered; (2) the determination of the surface of saturation; (3) following the progress of crystallisation, and determining the quantity of salt deposited; (4) the conditions under which there is re-solution of one of the salts at the invariant point. The problem is illustrated by reference to the double decomposition,

$$NaNO_3 + NH_4Cl = NH_4{\cdot}NO_3 + NaCl.$$

W. G.

Theory of Unimolecular Reactions. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 269—274).—A theoretical paper. The dependence of the specific reaction rate on temperature in dilute homogeneous systems can be fairly satisfactorily represented by the expression $k = se^{-Q/RT}$. The significance of Q and s is differently interpreted by different authors (Lewis, T., 1918, **113**, 471, and others). The true significance of these quantities is discussed in the present paper.

J. F. S.

Phenomena of the Ignition of Gaseous Mixtures by Induction Coil Sparks. JOHN DAVID MORGAN and RICHARD VERNON WHEELER (T., 1921, **119**, 239—251).

Oxidation and Luminescence of Phosphorus. I. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1921, **25**, 61—81).—It is assumed that when phosphorus vapour and oxygen are brought in contact the reaction proceeds with a velocity given by $V = kC_P^x . C_O^y$, where C_P and C_O are the concentrations of phosphorus vapour and oxygen. C_P is constant in contact with the solid, hence the velocity of oxidation is $V = k_1C_O^y$. Below 25° and above a certain partial pressure of oxygen, this is no longer valid, owing to the formation of an oxide film on the surface of the phosphorus. If the oxygen pressure is great enough, the reaction is forced to the surface of the solid phosphorus, which becomes covered with the oxide film. The film is destroyed by decreasing the partial pressure of the oxygen below a limiting value or by increasing the rate of volatilisation of the phosphorus. The limiting pressure, above which a protecting film is produced, is not constant, since any factor which diminishes the oxygen concentration or rate of diffusion, or increases the phosphorus vapour pressure or rate of diffusion, will increase the limiting pressure. The intermittent luminescence in the narrow critical region between the limiting

pressure and the glow pressure may be due to the periodic breaking down and re-formation of the oxide film. J. R. P.

Motion of Sound in Partly Dissociated Gases. A. Einstein (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 380—385).—The theory of the motion of sound in a partly dissociated diatomic gas is examined. The velocity of sound depends on the constants of the velocity of reaction, and the latter may be determined from the velocity of sound in the gas. J. R. P.

Thermal Decomposition of Gaseous Nitrogen Pentoxide: a Unimolecular Reaction. Farrington Daniels and Elmer H. Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 53—71).—The velocity of decomposition of gaseous nitrogen pentoxide has been determined at temperatures from 0—65°, using an all-glass apparatus. The manometer used has been previously described (A., 1920, ii, 485) as has also the method of preparing pure nitrogen pentoxide. The decomposition at all temperatures is shown to be unimolecular. The velocity constant has the following values at the different temperatures: 65°, 0·292; 55°, 0·0900; 45°, 0·0299; 35°, 0·00808; 25°, 0·00203; 25° (with solid present), 0·00191; 20°, 0·00117; 15° 0·000624; and 0°, 0·0000472. The large temperature coefficient of the reaction velocity showed that catalysis by the glass walls and diffusion was not a factor in the reaction; furthermore, the addition of glass wool with a large surface caused no change in the rate of reaction. The amount of nitrogen pentoxide taken was calculated from the pressure after complete decomposition. The results were corrected for the dissociation $N_2O_4 \rightleftarrows 2NO_2$ so that the system studied was

$$2N_2O_5 \rightarrow \underset{\substack{\uparrow\downarrow \\ 4NO_2}}{2N_2O_4} + O_2.$$

The critical increment E has been calculated and found to be independent of the temperature; it has the value 24,700 cals. J. F. S.

Photochemical Decomposition of Nitrogen Pentoxide. Farrington Daniels and Elmer H. Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72—81. Compare preceding abstract).—The photochemical decomposition of nitrogen pentoxide has been investigated at 0°. It is shown that the black body radiation from the vessel walls at 0° causes a reaction which is negligible in comparison with that produced by radiation received from a body emitting white light and not in equilibrium with the system. Calculations from the reaction velocity constants at different temperatures give 24,700 cals. for the critical increment, E. From the expression $E = Nh\nu$, λ is found to be $1{\cdot}16\mu$, which, according to the hypotheses of Perrin (A., 1919, ii, 177) and Lewis (T., 1918, **113**, 471), should be photochemically active in this case. It is shown, however, that light of this wave-length does not decompose nitrogen pentoxide within the limits of the present observations. Light in the region 400—460$\mu\mu$ accelerates the decomposition of nitrogen pentoxide, but this decomposition does not take place

unless the dioxide is present. The autocatalytic effect of nitrogen dioxide is negligible in the dark. Hypotheses to explain these facts are put forward, and their relation to theories connecting chemical action with radiant energy is suggested. J. F. S.

Law of Probability Applied to the Formation of Fats from Carbohydrates. EDGAR J. WITZEMANN (*J. Physical Chem.*, 1921, **25**, 55—60).—If the relative abundance of occurrence of the various fatty acids in plants is plotted against the number of carbon atoms, and the prominences corresponding with C_{12}, C_{24}, etc., are connected, a smooth curve symmetrical about the maximum ordinate corresponding with C_{18} is obtained, which has the form of the typical probability curve. This is said to support the hypothesis that the fatty acids are formed from carbohydrates containing chains of six carbon atoms. Three molecules of the latter, for example, are joined through their aldehyde groups, and by transposition and removal of oxygen from the resulting molecule a fatty acid containing C_{18} is formed. The less frequent occurrence of intermediate acids containing C_{10}, C_{14}, etc., may be due to their formation from higher unsaturated acids by loss of two or more carbon atoms, or by synthesis from short carbon chains. J. R. P.

The Activity of Water in Sucrose Solutions. W. E. GARNER and IRVINE MASSON (*Phil. Mag.*, [vi], 1921, **41**, 484—486).—The results of Jones and Lewis (T., 1920, **117**, 1125) are explained on the assumption that the increase of activity of the hydrogen ion is due to a virtual increase in the concentration of the sulphuric acid due to the inactivating effect of sucrose molecules on water molecules. This effect may consist in hydration of the sucrose, and in this case there would be an actual increase in the hydrion concentration in the free water. The water which is thus fixed by the sugar (changing from $10H_2O$ to $5H_2O$ per sucrose molecule) is not available as a solvent for the hydrogen ion or for gases, nor is it osmotically active. From the data of Jones and Lewis it appears that this water is nevertheless chemically active, since the rate of inversion is proportional to the total water present, and not merely to the free water—a fact which is said to be difficult to explain on any supposition other than the above. J. R. P.

Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts. VAN L. BOHNSON (*J. Physical Chem.*, 1921, **25**, 19—54).—Ferric salts accelerate the decomposition of hydrogen peroxide to a greater degree than sodium iodide in equivalent concentration. With dilute solutions of ferric chloride and nitrate the effect is proportional to the concentration; ferric sulphate is less active. The catalytic effect is explained by the intermediate formation of ferric acid: (1) $2FeR_3 + 3H_2O_2 + 2H_2O \rightleftharpoons 2H_2FeO_4 + 6HR$; (2) $2H_2FeO_4 + 3H_2O_2 \rightleftharpoons 2Fe(OH)_3 + 2H_2O + 3O_2$; (3) $2Fe(OH)_3 + 6HR \rightleftharpoons 2FeR_3 + 6H_2O$, in which (2) is a measurable reaction. Constants were obtained for the unimolecular reaction. The specific reaction velocity decreases as the reaction proceeds, owing to hydrolysis of the catalyst. Colloidal ferric hydroxide or

basic salts have no catalytic effect. Addition of acid retards the reaction, apparently by reducing the concentration of the intermediate product. Salts having an ion in common with the catalyst retard the decomposition by decreasing the dissociation of the catalyst. Mercuric chloride has very little influence; sodium sulphate, acetate, and formate delay the reaction, apparently owing to hydrolysis of the resulting ferric salts. A mixture of ferric sulphate with ferric chloride or nitrate does not accelerate the reaction to so great an extent as would be indicated by the sum of the separate effects. Cupric sulphate accelerates the action of ferric sulphate. Alcohol, which is oxidised by the ferric salt, acts anti-catalytically owing to the formation of acetic acid. Glycerol, sucrose, gelatin, carbamide, and acetamide also act anti-catalytically.

J. R. P.

The Catalytic Decomposition of Hydrogen Peroxide by Electrosols and Electrogels of Platinum. ANTONIO DE GREGORIO Y ROCASOLANO (*Anal. Fís. Quím.*, 1920, **18**, 361—367).—The author criticises the hypothesis of Bredig that the catalytic decomposition of hydrogen peroxide is unimolecular. Using electrosols of platinum of varying concentrations (0·001—0·003%), the decomposition has been followed over periods up to 10,080 minutes. It is shown that, applying the results obtained to the usual formula $K = 1/t \log a/a - x$, the values of K show a steady diminution with increasing time.

Applying the results to a modified formula used elsewhere in studying the catalytic decomposition of hydrogen peroxide by hæmase, the values of K showed a similar lack of constancy.

Plotting the values of K obtained against the time, it is shown that in the later stages the curve becomes almost parallel to the time axis. In other words, the value of K reaches a constant, and the reaction becomes unimolecular.

In order to confirm this, the corresponding platinum gels, obtained by drying the sols at the ordinary temperature, were used as catalysts. In all cases the reactions were found to be truly unimolecular. This was also the case where fresh hydrogen peroxide was added after the reaction had reached the unimolecular stage.

It is supposed that the disperse phases of electrosols of platinum consist of solid solutions of oxygen in platinum. The catalytic activity of a sol is proportional to the oxygen concentration in the disperse phase. This concentration of oxygen diminishes as the reaction proceeds, and reaches a minimum in the later stages when the reaction becomes unimolecular.

G. W. R.

Influence of Mercury, Sulphur, Arsenic, and Zinc on the Catalytic Activity of Platinum. EDWARD BRADFORD MAXTED (T., 1921, **119**, 225—233).

Periodic System, Atomic Structure, and Radioactivity. FRANZ URBACH (*Physikal. Zeitsch.*, 1921, **22**, 114—119).—A conception of the atomic structure, based on the relationships apparent from the periodic system, is put forward. This idea leads to an

explanation of the many regularities of the periodic system. A consideration of the phenomena of radioactive disintegration in connexion with the Kossel valency hypothesis (A., 1916, ii, 243) leads to an interpretation of other radioactive phenomena, and to an explanation of the eighth group of the periodic system and to a possibility of explaining the existence of the elements of the rare earths. J. F. S.

The Structure of the Molecule and Chemical Combination. (SIR) J. J. THOMSON (*Phil. Mag.*, 1921, [vi], **41**, 510—544).—It is assumed (cf. *Phil. Mag.*, April, 1919) that in the atom the electrons are in equilibrium under their mutual repulsions and the attractions exerted upon them by the positive charges. The repulsions between electrons are supposed to follow the inverse square law, but the force between the electron and the positive charge is more complicated and varies with the distance r according to a law $F(c/r)$ where c is a length. When r is very large or very small compared with c, $F(c/r)$ reduces to $1/r^2$, but when r is comparable with c the force is no longer of simple type, but vanishes at certain distances, changing from attraction to repulsion, or vice versa. This arrangement is preferred to electrons describing orbits under forces varying as the inverse square law, because in the latter each electron must have a separate and isolated orbit if the system is to be stable and the model becomes too complicated to be of assistance. The scattering of light is also not in accordance with electrons describing orbits.

The arrangement of electrons around the central positive charge is next considered. If there is only one electron it must be at one of the places where the force exerted by the central charge vanishes, and the condition of stability requires that the force must become attractive when the electron is displaced away from the centre and repulsive when it is displaced towards the centre. The condition of equilibrium for two electrons is that they shall be situated so that the centre is midway between them, and the repulsion between them is equal to the attraction exerted by the centre on either. Three electrons arrange themselves at the corners of an equilateral triangle, four at the corners of a regular tetrahedron, and so on. The electrons are on the surface of a sphere with the positive charge at the centre. For any number of electrons, these must be symmetrically placed so that the force exerted on any electron by any other is along the radius and its magnitude the same for all. This equilibrium will not be stable unless another condition is satisfied, and the limitation thus imposed determines the structure of the atom or molecule. It is that the attraction due to the central charge is greater than the repulsion due to other electrons when one electron is displaced outwards by a small distance from its equilibrium position. It is shown in this way that, although there may be equilibrium positions with large numbers of electrons if the central charge is proportional to the number of electrons, the condition of stability is satisfied only by a limited number of electrons, provided that the central charge

is not to exceed the sum of the charges on the electrons. If the law of force is $F(c/r) = E(1 - c/r)/r^2$, where E is the central charge, this maximum number of electrons is eight, independent of c, if the electrons are at the corners of a regular polyhedron. It is five if the electrons are in a ring.

The cube is not the stable arrangement of eight electrons; this is a twisted polyhedron with eight triangular faces and two four-sided ones. Two such polyhedra may be placed in contact so as to have two, three, or four corners in common. When there are more than eight electrons on the surface of a sphere the positive charge at the centre becomes greater than the charges on the electrons, and this governs the structures of atoms and molecules, which must be electrically neutral.

Atoms may therefore exist with from one to eight electrons on the surface of a sphere surrounding a positive charge equal to the sum of the charges on the electrons. If the central charge is nine, eight electrons will form a spherical shell concentric with the central charge, and one electron will go outside to find a position of stable equilibrium. The external layer of this atom will contain one electron, and in this respect will resemble the atom with unit positive charge and one electron. If the atom contains ten electrons there will be two outside the shell, and so on. When the number of electrons outside the first shell becomes eight they compose a second complete shell, and so on. There will be a periodicity of the number of electrons in the outer shell, this rising from one to eight, then dropping to one again, and so on. So far as properties depending on the outer layer are concerned, the elements will exhibit periodicity similar to that expressed in the periodic law.

The number of elements included in a period may be greater than eight, in the case of elements of high atomic weight. The addition of one unit to the positive nuclear charge may lead to one additional electron leaving the outer shell and entering a shell of the innermost layer. The two atoms will have different atomic weights and different central charges, but equal numbers of electrons in the outer layers, so that their properties which depend on the outer layer (presumably including valency) will be common. When there are a great number of electrons in many layers it may require the addition of several electrons before a new electron finds its way to the outer layer, and there may be a considerable number of elements with different atomic weights, but very similar chemical properties, such as the transitional elements and the elements of the rare earths. The number of electrons in the outer layer is supposed to be equal to the number of the group in which the element occurs in the periodic table.

It is shown that an atom with seven electrons in the outer shell, such as fluorine, may have the same valency as an atom with only one, such as sodium, and that an atom may possess two valencies, the sum being always equal to eight. The existence of active valencies of seven in alkali metals is, however, not probable on the theory. The freedom of motion of the electrons is of importance in connexion with the attraction which the atom is likely to experience

from other atoms. A mobile electron will move round to face a positive atom.

The distance of the outer ring of electrons from the centre of the atom is shown to diminish in atoms of a period from that of least to that of greatest atomic weight. It increases again abruptly when a new period begins, only to fall throughout the period. This differs from Lothar Meyer's generalisation, in which the minimum atomic volumes came at the middle of the periods, but is in agreement with the results of W. L. Bragg (A., 1920, ii, 537).

Molecules are assumed to be formed by the electrons of the atoms acting as couplings; each unit valency bond requires two electrons, one belonging to each atom. A double bond is represented by four electrons arranged at the corners of a square at right angles to the line joining the atomic centres. More complicated cases are discussed. Molecules may have transitory existence which violate the ordinary principles of valency, for example, CNe, NF, NOH_2, etc. The molecules which survive are those showing the smallest tendency to attract other molecules—" the law of survival of the unattractive."

The similarity in physical properties of carbon monoxide and nitrogen is referred to, and a distinction drawn between carbon monoxide and the carbonyl radicle. In the latter two of the four electrons of the carbon atom unite it to the oxygen, making up with the six electrons of the latter an eight-electron cell around the oxygen, leaving two electrons free. The benzene molecule may be represented as composed of six cells and thirty electrons. The cells may be in contact round a ring with threefold contact between each two. As the opposite triangular faces of the twisted cell which is the stable configuration for eight electrons are inclined, this packing could be done without introducing much strain, and the result would be a completely symmetrical structure representing the so-called " centric formula." A representation of the Kekulé formula is also possible; three sets of pairs of cells are taken, the cells in one pair having fourfold contact with each other, but only double contact with a cell of a neighbouring pair.

The evidence from positive rays is discussed in detail, and the existence of charged atoms and molecules and the magnitudes of the charges are shown to be in agreement with the theory.

The configuration of the molecule may be inferred from the scattering of light. The light scattered from an electron or a perfectly symmetrical body, such as a spherical molecule, is completely polarised in a direction at right angles to the incident beam. That scattered from an imperfectly symmetrical body is not completely polarised, and the ratio of the minimum to the maximum intensity as seen through a Nicol may be taken as an indication of the deviation of the scattering body from sphericity. In this way it is shown that the symmetry decreases from argon to nitrogen, abruptly to oxygen, and again abruptly to carbon dioxide and nitrous oxide. The nitrogen molecule appears to contain only one cell, the oxygen molecule two, and carbon dioxide and nitrous oxide three cells. Other properties are discussed. J. R. P.

Theory of Auxiliary Valencies and Water of Crystallisation. H. T. F. RHODES (*Chem. News*, 1921, **122**, 85—87, 97—99).—A theoretical discussion of the constitution of crystal hydrates. After a discussion of Werner's co-ordination hypothesis, the author proposes ring structures for the molecules of salts with water of crystallisation which are similar to those for complex salts put forward by Friend (T., 1908, **93**, 1006).—An examination of a list of crystalline hydrates shows that 4% have $1H_2O$ of crystallisation, 6%, $2H_2O$, 8%, $3H_2O$, 16% 4 and $8H_2O$, 19%, 5 and $10H_2O$, 38%, 6, 7, and $12H_2O$; 4%, $9H_2O$; 2%, $15H_2O$, and 3%, $18H_2O$.

J. F. S.

Application of the Law of Hydrolysis to the Determination of Molecular Weights. H. COLIN and (MLLE) A. CHAUDUN (*Compt. rend.*, 1921, **172**, 278—280).—From a study of the hydrolysis of sucrose, raffinose, and gentianose by sucrase it is shown that if a group of substances of molecular weights, M_1, M_2, M_3 . . . M_n, are all hydrolysed in an identical manner by the same ferment, and the weights of these different substances capable of fixing equal quantities of enzyme are given by a_1, a_2, a_3 . . . a_n, then

$$a_1/M_1 = a_2/M_2 = a_3/M_3 = \ . \ . \ . = a_n/M_n.$$

W. G.

Glass Autoclave. SCHMIDT (*Zeitsch. angew. Chem.*, 1921, **34**, 37).—An autoclave constructed entirely of glass is mentioned which may be used for pressures up to 4 atmospheres. The construction appears from a drawing to be similar to that of the ordinary metal autoclave. The apparatus is fitted with a valve which must be moistened with liquid paraffin, and a tap is attached whereby gas (carbon dioxide or nitrogen) under pressure may be admitted. J. F. S.

An Automatic Syphon. C. J. PELLE (*Chem. Weekblad*, 1921, **18**, 127).—This device, due to P. H. Bon, consists in fusing to the end, *a*, of one limb of an ordinary syphon tube a considerably wider concentric tube, *b*. The lower end of *b* is closed or sealed except for an opening much smaller than the diameter of *a*. A small opening, *c*, is made in the inner tube, *a*, just below the point at which *b* is fused on. When the limb is plunged into fluid, the latter ascends in *a* much more quickly than in *b*, since the opening in the latter is so small, and closes the opening, *c*, so that air is enclosed in *b* under pressure, and assists the liquid to rise in *a*.

S. I. L.

Inorganic Chemistry.

The Rectilinear Diameter of Hydrogen. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1921, **172**, 261—263).—The authors have determined the density curves of hydrogen for the liquid and the saturated vapour at the same temperatures between the critical point, $-239{\cdot}91^{\circ}$, and the b. p., $-252{\cdot}66^{\circ}$. The ordinate of the diameter is given by $y = -0{\cdot}063510 - 0{\cdot}000394020\theta$. The angular coefficient of the diameter is $d = -0{\cdot}00039402$. The formula of the diameter gives for the critical density at $-239{\cdot}91^{\circ}$ $\Delta = 0{\cdot}03$, the critical coefficient being $R\odot\Delta/\pi = 3{\cdot}276$. The deviations of the diameter are for the most part small, and show that hydrogen obeys the law of the rectilinear diameter. W. G.

Some Properties of Selenium Oxychloride. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1921, **43**, 29—35).—A number of the properties of selenium oxychloride ($SeOCl_2$) have been investigated. It is a nearly colourless liquid, b. p. $176{\cdot}4^{\circ}$ at 726 mm., m. p. $8{\cdot}5^{\circ}$, refractive index at 20°, $1{\cdot}6516$, specific conductivity $9{\cdot}6 \times 10^{-4}$ at 28°. It absorbs all light up to $\lambda = 4050\mu\mu$, and is completely miscible with carbon tetrachloride, chloroform, carbon disulphide, and benzene, no chemical action taking place in any case. Saturated aliphatic hydrocarbons are immiscible with selenium oxychloride at the ordinary temperature, but when a mixture of the higher paraffins (vaselin) and selenium oxychloride are heated to 150—160° complete miscibility is obtained. Sulphur, selenium, and tellurium dissolve in cold selenium oxychloride, but when heated, reactions take place, in the case of sulphur the products are selenium monochloride, sulphur monochloride, and sulphur dioxide, tellurium is converted into the tetrachloride. Red phosphorus attacks cold selenium oxychloride with development of heat and light, whilst yellow phosphorus reacts explosively. Bromine and iodine dissolve in selenium oxychloride to produce very active solutions, which are coloured reddish-brown and violet respectively. Boron, silicon, and carbon are not attacked by the oxychloride. Most of the metals react with the oxychloride to form the chloride of the metal and selenium monochloride, thus aluminium, zinc, bismuth, and tin react readily, calcium, copper, magnesium, chromium, lead, nickel, arsenic, cadmium, cobalt, gold, and platinum are slowly attacked, potassium reacts explosively, whilst sodium is not affected by the oxychloride even when it is distilled over the metal. Iron reacts slowly with the cold oxychloride, but the reaction is accelerated on heating, titanium is only acted on at high temperatures, and there is no action with tungsten. Selenium oxychloride dissolves selenium dioxide, arsenic trioxide, vanadium pentoxide, and molybdenum trioxide; in the last three cases a reaction takes place. A reversible photochemical reaction occurs with the solution of molybdenum trioxide; in bright light the solution becomes indigo-blue in a few minutes,

and this when kept in subdued light fades to pale yellow in a few hours. The oxides of aluminium, thorium, the rare earths, titanium, zirconium, niobium, and tantalum are not attacked, but uranium oxide is slowly attacked at ordinary temperatures. Tellurium is dissolved, but may be regained by distilling the solvent. Sulphur trioxide dissolves in the oxychloride to form a thick, heavy solution, which is a powerful solvent. This mixture will dissolve the oxides of aluminium, chromium, the rare earths, titanium, niobium, molybdenum, vanadium, and uranium, but will not dissolve the oxides of zirconium or tungsten, and dissolves tantalum oxide but slightly. The reactions of selenium oxychloride with a number of carbonates, sulphides, carbides, and other compounds are described. It is remarkable that calcium hydride, carbide, and phosphide do not react with cold selenium oxychloride, but the two latter compounds react slowly on boiling. Barium sulphate is peptised by selenium oxychloride, a gel is formed much like aluminium hydroxide, which is changed to the ordinary form by treatment with water. Chromium trioxide or potassium dichromate dissolves in selenium oxychloride to form a red solution, which on heating evolves chromyl chloride. Saturated aliphatic hydrocarbons are only slowly attacked even on heating, whilst unsaturated aliphatic hydrocarbons and terpenes react violently with the oxychloride. Benzene hydrocarbons form physical mixtures. Protein materials, such as hair, silk, and leather, dissolve in the cold oxychloride, but cellulose is neither dissolved nor attacked. Vegetable and fish oils are acted on much in the same way as by sulphur monochloride; with linseed oil a rubber-like mass is produced. Menhaden oil reacts with selenium oxychloride to form a waterproof rubber-like mass. Pure rubber, vulcanised rubber, and vulcanite are all chemically attacked by the oxychloride. Gums, resins, shellac, dried paints, lacquer, agar, celluloid, gelatin, and glue are dissolved by cold selenium oxychloride. Natural asphalts, resins, and bitumens dissolve with ease in selenium oxychloride in the cold when they are unsaturated, but substances like ozokerite behave like the paraffins. With coal and carbon selenium oxychloride extracts the bituminous and resinous materials, and leaves a carbonaceous residue. In handling selenium oxychloride the same care is used as with any other corrosive liquid; it has no other physiological action beyond that of the action of the hydrochloric acid produced when its vapours are hydrolysed in contact with the mucous membrane. J. F. S.

The System, Iodine–Tellurium. Study of the Vaporisation. A. Damiens (*Compt. rend.*, 1921, **172**, 447—450).—A study of the vaporisation of different mixtures of iodine and tellurium tetraiodide in a vacuum confirms the results previously obtained from a thermal study of the system, iodine–tellurium (this vol., ii, 110). W. G.

Photoelectric Photometry of the Luminosity of Active Nitrogen. E. von Angerer (*Physikal. Zeitsch.*, 1921, **22**, 97—102).—A method is described whereby by means of a photo-

electric cell, a variable feeble light intensity may be measured from second to second. It is shown that the lag of the photoelectric cell is so slight that for such purposes it may be neglected. The arrangement described has been used to determine the rate at which the luminosity of active nitrogen disappears. A glass globe 47 cm. diameter was filled at a suitable pressure with chemically pure nitrogen and used as an electrodeless tube. After the current was broken it was found that the bulb glowed for two and a half minutes when strongly excited, and in any case it was possible to read a watch for fifteen seconds after the current was switched off. It is shown that the reciprocal of the light intensity is practically proportional to time which has elapsed from the breaking of the exciting circuit, which implies that the reaction accompanying the luminosity is bimolecular. J. F. S.

Demonstration of the After-glow of Active Nitrogen by Means of an Electrodeless Ring Current. J. Zenneck (*Physikal. Zeitsch.*, 1921, **22**, 102—103. Compare preceding abstract).—An electrodeless globe 46·5 cm. diameter and filled with chemically pure nitrogen is encircled by a simple wire circuit 47·5 cm. long, which is connected with four large Leyden jars and a spark gap. The system is fed by a Boas resonance induction apparatus for fifty-period alternating current. Using such an arrangement, the after-glow is visible for about thirty seconds. The glow is very intense and of an orange-yellow colour at first, which slowly changes to a greenish-yellow colour. J. F. S.

The Actual State of the Synthesis of Ammonia by Hyperpressures. Georges Claude (*Compt. rend.*, 1921, **172**, 442—444. Compare A., 1920, ii, 30, 173).—The apparatus previously described (*loc. cit.*) is modified so as to carry out the compression of the mixed gases in one stage and materially to increase the yield. W. G.

The Fusion of Carbon. Eugen Ryschkewitsch (*Zeitsch. Elektrochem.*, 1921, **27**, 57—64).—The carbon electrodes of a resistance furnace, after a run of from eight to twelve hours, showed unquestionable signs of having partly melted at the points of contact with the graphite which served as the resistance of the furnace. At the end of the run both the resistance material and the electrode ends were practically pure graphite, containing 99·9% of carbon. The results of other investigators on the fusibility of carbon, Moissan, Despretz, La Rosa, and Lummer, are discussed. [Compare *J. Soc. Chem. Ind.*, 1921, 178A.]
E. H. R.

Topochemical Reactions. Formation of Carbon at Contact Substances. V. Kohlschütter and A. Nägeli (*Helv. Chim. Acta*, 1921, **4**, 45—76. Compare A., 1919, ii, 151, 152, 156).—The authors have investigated the nature of the carbon deposited when carbon monoxide is passed through a tube containing a metallic accelerator heated at 500° (compare Gruner,

A., 1871, 798; Schenck and Zimmermann, A., 1903, ii, 423; Schenck and Heller, A., 1905, ii, 519, 526; Smits, A., 1906, ii, 71). The accelerators employed comprised powdered nickel and cobalt, powdered and reduced iron, electrolytic nickel, nickel filings, rolled metallic foil, and both smooth and rough electrolytic deposits of various metals.

The structure of the carbon separated is found to be influenced by the character of the contact metal, the temperature of the reaction, and the state of subdivision of the accelerator. Cobalt yields a graphitic carbon of markedly different nature from that obtained with iron or nickel; the similarity of the results obtained with electrolytic and powdered cobalt indicates a specific action of the metal. Neither with reduced nor with powdered iron is the formation of graphite favoured by raising the temperature of the reaction; increase in the degree of subdivision of this metal does, however, favour the development of the graphitic type.

In comparison with the carbon of electrolytic deposits which exhibits strongly graphitic properties, that deposited on powders, with the exception of powdered cobalt, more nearly resembles soot in appearance and behaviour. The view that a continuous gradation exists between the different forms of carbon is thus supported, and it is further evident that, under similar external conditions, the formation of one or another product may be obtained from one and the same chemical reaction merely by alteration of the structure of the locality of the reaction. T. H. P.

The Combustion of Carbon in the Presence of Oxides. E. BERGER and L. DELMAS (*Bull. Soc. chim.*, 1921, [iv], **29**, 68—77).—An examination of the behaviour of two types of carbon, when intimately mixed with small amounts, not exceeding 4%, of different metallic oxides, and heated to their ignition points. A certain number of these oxides facilitate the combustion of the carbon in air. A certain number of other oxides cause a diminution in the proportion of carbon monoxide produced in the combustion of the carbon alone. Among the most active are those which are known as good catalysts for various oxidation processes.

W. G.

Absorption of Carbon Monoxide by Cuprous Ammonium Carbonate Solutions. WM. R. HAINSWORTH and E. Y. TITUS (*J. Amer. Chem. Soc.*, 1921, **43**, 1—11).—The volume of carbon monoxide absorbed by stated volumes of cuprous ammonium carbonate solution has been determined for various concentrations of the solution at temperatures, 1°, 11°, 40°, 50°, and 60°, and at various pressures. The absorption capacity of a solution having a given cuprous content is dependent on the free ammonia content of the solution and the partial pressure of the carbon monoxide above it, as well as the concentration of the cuprous copper. Under the experimental conditions the absorption takes place with the formation of an unstable compound which probably contains one molecule of carbon monoxide to each gram-atom of cuprous copper.

$$Cu_2(NH_3)_{2n}CO_3 + 2CO + 4H_2O = Cu_2(NH_3)_{2n}CO_3,2CO,4H_2O.$$

Cupric copper is reduced to cuprous copper fairly rapidly by carbon monoxide according to the equation $2Cu(NH_3)_4CO_3 + CO + 2H_2O = Cu_2(NH_3)_{2n}CO_3 + 2(NH_4)_2CO_3 + (4 - 2n)NH_3$, whilst the reduction of cuprous copper to metallic copper is comparatively a much slower process, and occurs according to the equation $Cu_2(NH_3)_{2n}CO_3 + CO + 2H_2O = 2(NH_4)_2CO_3 + 2Cu + (2n - 4)NH_3$. Small amounts of oxygen present in the gaseous mixtures, from which the carbon monoxide is to be removed, prevent the precipitation of copper and increase the absorption capacity of the solution. The carbon monoxide can be almost completely removed from the absorption solution by heating it at 75° at atmospheric pressure in an inert atmosphere, and the solution may then be used again for further absorption of carbon monoxide. J. F. S.

Carbon Dioxide in Water of the Gulf of Mexico. ROGER C. WELLS (*U.S. Geo. Sur., Prof. Paper*, 120A, 1918, pp. 1—16).—The total carbon dioxide in the sea-water of the Gulf of Mexico increases with the depth, that is, with decreasing temperature, and the amounts found are very near, though slightly below, those required for equilibrium with atmospheric carbon dioxide. Determinations of the total quantity of base present as carbonate and hydrogen carbonate were also made; this quantity apparently increases slightly with decreasing temperature. An exact computation of the "free" carbon dioxide in the water was not possible, but the results indicated that no appreciable error is made when the total carbon dioxide found is expressed as a mixture of carbonate and hydrogen carbonate. E. H. R.

Silicic Acid Gels. ROBERT SCHWARZ (*Kolloid Zeitsch.*, 1921, **28**, 77—81).—The solubility of silicic acid in ammonia has been studied. It is shown that a solution of silicic acid in ammonia may be separated into two fractions, one which will pass through the finest ultra-filter and therefore consists of molecular disperse silicic acid, that is, ammonium silicate, and the other, which is retained by the ultra-filter and consists of colloidal silicic acid. The amount of dissolved silicic acid has been estimated at various periods after solution, and it is found that the amount increases with time; thus eight hours after solution 30·6% of a given silicic acid gel was dissolved, 16·0% was in the colloidal condition, and 53·4% was undissolved, but in ninety-five hours 63·9% was dissolved, 8·1% was in colloidal solution, and 28·0% was undissolved. From which it is deduced that the colloidal solution is the first stage of the solution and that the true solution is a secondary reaction following the formation of the colloidal solution. J. F. S.

Measurement of Vapour Pressures of certain Potassium Compounds. DANIEL JACKSON and JEROME J. MORGAN (*J. Ind. Eng. Chem.*, 1921, **13**, 110—118).—A method described by von Wartenberg (A., 1912, ii, 1137; 1913, ii, 47) was adapted to the determination of the vapour pressures of potassium compounds with the following results, the values being given in mm. of mercury :

Hydroxide, 8 mm. at, 795°. Chloride, 1·54 mm., at 801°; 8·33 mm. at 948°; 24·1 mm. at 1044°. Carbonate, 1·68 mm. at 970°; 5·0 mm. at 1130°. Sulphate, 0·4 mm. at 1130°. Natural silicates 0 mm. at 1130—1335°.

From the results obtained for potassium chloride, together with the boiling point of this compound as given by Borgstrom, the Nernst vapour pressure formula for potassium chloride has been calculated to be:

$$\text{Log}\ P = -5326/T + 1{\cdot}75 \log T + 0{\cdot}000511\ T - 0{\cdot}7064.$$

W. P. S.

Crystal Structures of the Ammonium Haloids Above and Below the Transition Temperatures. Guy Bartlett and Irving Langmuir (*J. Amer. Chem. Soc.*, 1921, **43**, 84—91).—Ammonium chloride, bromide, and iodide are polymorphous and have well-defined transition temperatures. *X*-ray crystal analysis by Hull's method (A., 1919, ii, 1168) shows that the high temperature form of each of these substances has a simple cubic structure like sodium chloride, each ion being surrounded by six equidistant ions of the opposite polarity. The ordinary or low temperature forms of the chloride and bromide show a centred cubic structure, each ion being surrounded by eight equidistant ions of the opposite polarity, arranged as the corners of a cube about its centre. These results furnish confirmatory evidence that the ammonium ion has tetrahedral symmetry, while the alkali and halogen ions are cubic in shape. Low temperatures, high pressures, and anions of small atomic volume cause the shape of the ammonium ions to be a factor of predominating importance in determining the crystal structure. High temperatures, low pressures, and anions of large volume make the shape of the ammonium ion of relatively less importance, so that under these conditions ammonium salts tend to become isomorphous with the corresponding potassium salts. The following data have been obtained: Ammonium chloride, at 20°, distance between like ions l_1, 3·859° Å.U., distance between unlike ions l_2, 3·342°Å.U., density (calculated) D 1·536; at 250°, l_1, 4·620 Å.U., l_2 3·266 Å.U., D 1·265; ammonium bromide, at 20°, l_1, 3·988, l_2, 3·453, D, 2·548; at 250°, l_1, 4·88, l_2, 3·45, D, 1·972; ammonium iodide, at 20°, l_1, 5·090, l_2, 3·62, D, 2·563. J. F. S.

Distribution of a Strong Electrolyte between Water and Benzene. Arthur E. Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254—268).—The molecular weight of silver perchlorate has been determined in benzene solution and it is shown that this salt exists in benzene solution as single molecules as well as in polymerised molecules of double and triple molecular weight. The average molecular weight up to a concentration 0·14*N* is expressed by the equation $MW = C^{0{\cdot}17}/1{\cdot}571 \times 10^{-3}$. In benzene solution there is no electrolytic dissociation, except possibly of the same order as that of pure water. Silver perchlorate is soluble in chlorobenzene, glycerol, acetic acid, toluene, and nitrobenzene. It is soluble in water at 25° to the extent of 2386 grams per litre of water, and in

anhydrous benzene to the extent 45·29 grams per litre of solution. The saturated aqueous solution has $D_{4°}^{25°}$ 2·806, whilst the saturated benzene solution has $D_{4°}^{25°}$ 0·9053. A method is put forward for calculating the concentration of the three different species of silver perchlorate molecules in benzene solution, and curves are drawn for these concentrations. Distribution experiments show that water extracts the salt completely from its benzene solution up to a concentration 2·3*N* in the aqueous layer. The experiments are interpreted as evidence that silver perchlorate, apparently a typical salt, is completely ionised in water at higher as well as at low concentration. J. F. S.

Crystallisation in Ternary Systems of the Chlorides of Univalent and Bivalent Metals. II. TH. LIEBISCH and EHR. VORTISCH (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 426—442. See A., 1917, ii, 248).—Previous investigations are extended by a consideration of the formation of solid solutions. The systems $NaCl–SrCl_2–BaCl_2$ and $KCl–SrCl_2–BaCl_2$ were investigated and the results shown in the form of curves. J.R.P.

Devitrification of Glass : A Surface Phenomenon : Repair of Crystallised Glass Apparatus. ALBERT F. O. GERMANN (*J. Amer. Chem. Soc.*, 1921, **43**, 11—14).—The devitrification of glass in a blowpipe flame is not due to the formation of crystal nuclei within the mass of the glass, but is a surface phenomenon due to the expulsion of water and carbon dioxide, and possibly when the glass is heated for a long time to the volatilisation of sodium oxide. To prevent such devitrification in old glass, it is sufficient to remove the surface layer by washing with diluted hydrofluoric acid solution before heating it. Old apparatus which has been broken may thus be repaired if the places to be heated are thoroughly washed with diluted hydrofluoric acid. J. F. S.

Reactions producing Magnesium. CAMILLE MATIGNON (*Compt. rend.*, 1921, **172**, 381—383).—The following three reactions are suggested as possible methods of preparation of magnesium :—

(1) $MgCl_{2\,sol} + CaC_{2\,sol} = CaCl_{2\,sol} + 2C_{sol} + Mg_{sol} + 22{\cdot}4$ cal.
(2) $MgO_{sol} + CaC_{2\,sol} = CaO_{sol} + 2C_{sol} + Mg_{sol} - 8{\cdot}4$ cal.
(3) $MgOMgCl_{2\,sol} + 2CaC_{2\,sol} = CaOCaCl_{2\,sol} + 4C_{sol} + 2Mg_{sol} - 2{\cdot}2$ cal.

Taking into account the heat of vaporisation of magnesium, it is shown that the absorption of heat per atom of magnesium volatilised is least for the first reaction and greatest for the second. It is possible to obtain magnesium by these methods, but reaction (2), carried out with a calcined dolomite, only proceeded very slowly even at 1300°. Reaction (1) involves the preparation of anhydrous magnesium chloride, which is a delicate and costly process. Attempts to apply these processes on a semi-industrial scale were not successful. W. G.

The Crystal Structure of Magnesium Oxide. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1921, [v], **1**, 138—152).—Laue photographs and *X*-ray spectrum measurements were made on

crystals of magnesium oxide, and the results were analysed with the help of the theory of space groups (this vol., ii, 245) in the hope of obtaining a unique solution of the structure of the crystals. The *X*-ray spectrum measurements do not settle the number of chemical molecules in the space unit, the alternatives being 4 and 32, and at the same time the class of symmetry is left in doubt. If the symmetry is holohedral cubic, the only possible simple solution is a structure similar to that of sodium chloride. Certain groupings showing tetartohedral symmetry, and some more complicated holohedral arrangements with thirty-two molecules associated in the unit would, however, be indistinguishable from the sodium chloride grouping with the experimental means at present available.

E. H. R.

Crystalline Magnesium Carbonate. T. C. N. BROEKSMIT (*Pharm. Weekblad,* 1921, **58**, 210—212).—The amorphous precipitate obtained by addition of sodium carbonate to magnesium sulphate in solution, said in the literature to be a basic carbonate, is found to become crystalline after a time. Exactly similar crystals are obtained from calcium salts under the same conditions. The compound may be that obtained by Schmidt by keeping the clear solution obtained by passing carbon dioxide into a suspension of amorphous magnesium carbonate, when crystals said to have the composition $MgCO_3,3H_2O$ separated in needles. The same crystals are obtained if potassium carbonate or hydrogen carbonate or ammonium carbonate is used, and it is shown that the compound is not a double salt. S. I. L.

Coloration of Zinc Sulphide by the Action of Light. YÛSHICHI NISHIZAWA (*J. Tokyo Chem. Soc.*, 1920, **41**, 1054—1064).—Zinc sulphide is tinged with light brown or light grey colour by exposure to light or by heating at 60—70°. The coloration is promoted by the presence of magnesium chloride or sulphate, zinc sulphate, or calcium chloride or sulphate, whilst the presence of a minute quantity of the following substances : multivalent alcohols, sugars, starch, oxalic acid, tartrates magnesium hydroxide, etc., inhibits the change. O'Brien (A., 1915, ii, 98) ascribed the coloration to the decomposition of zinc sulphide into zinc and sulphur, but samples which have not been coloured by exposure to light also yield zinc when treated with acetic acid. The author attempted to detect free sulphur in coloured samples, but without success, and suggests the cause of the colour to be the polymerisation of zinc sulphide, this being probable from the position of zinc in the periodic table. Lithopone can be made light-proof by mixing it with reagents such as those mentioned above. K. K.

Phosphorescence and Fusion of Sulphides of the Second Group, particularly Zinc Sulphide. ERICH TIEDE and ARTHUR SCHLEEDE (*Centr. Min.*, 1921, 154—158).—A further account of work already published (A., 1920, ii, 723, 757).

E. H. R.

Cuprous Oxide obtained by Reduction. V. V. SARMA (*Chem. News*, 1921, **122**, 99—100).—The yellow substance formed by reduction of an alkaline cupric salt with dextrose does not appear to be pure cuprous oxide. It contains a considerable amount of cuprous hydroxide which persists even after heating at 110°. On boiling the yellow substance with water a small portion remains suspended after boiling is discontinued, whilst most of it immediately settles as a granular powder. The heavier portion is not so bright in colour as the lighter one. When a drop or two of sulphuric acid is added to the lighter suspension it dissolves, giving a clear, colourless solution, which remains colourless on the addition of ammonia and only turns blue on keeping in the air. On treating the heavier portion with sulphuric acid it gives a blue solution of cupric sulphate and leaves metallic copper. When the yellow powder is shaken with ether a small portion dissolves and gives a bluish-green solution, and the powder loses its brightness and becomes dull yellow in colour. On heating the yellow substance gently in a tube, a thin, green coating is formed in the cooler parts of the tube and red cuprous oxide is left behind. It is held that the yellow product contains in addition to cuprous oxide 2—3% of water and an appreciable quantity of cuprous hydroxide. If sucrose is used instead of dextrose only red cuprous oxide is formed, irrespective of the temperature and method of reduction.

J. F. S.

Fractional Precipitation. PIERRE JOLIBOIS, ROBERT BOSSUET, and CHEVRY (*Compt. rend.*, 1921, **172**, 373—375).—Using the apparatus previously described (A., 1920, ii, 107, 112), the authors have followed the different phases in the fractional precipitate of a solution containing copper and silver nitrates by sodium hydroxide, and of a solution containing nickel and cobalt chlorides by the same reagent. It is shown that, in the first case, none of the silver is precipitated as silver hydroxide until sufficient sodium hydroxide has been added to precipitate the whole of the copper. Thus the fractionation is quantitative. In the second case the fractionation is imperfect. The precipitate is always richer in nickel than in cobalt.

W. G.

Gallium. Its Electrolytic Behaviour, Purification, Melting Point, Density, Coefficient of Expansion, Compressibility, Surface Tension, and Latent Heat of Fusion. THEODORE W. RICHARDS and SYLVESTER BOYER (*J. Amer. Chem. Soc.*, 1920, **43**, 274—294).—The purification of gallium, its electrolytic behaviour, and several of its physical constants have been investigated. It is shown that the single electrode potential of gallium is not easily reproducible at a constant value. It reached as a maximum only $-0{\cdot}30$ volt in $0{\cdot}1N$ solution (the calomel electrode being taken as $+0{\cdot}56$ volt), apparently placing gallium between indium and zinc in the electrochemical series. On the other hand, gallium is distinctly more difficult to precipitate electrolytically from acid solutions than zinc. From this behaviour gallium might be expected

to have a single electrode potential of at least -0.7. It may be precipitated in weakly acid solutions if a sufficiently large current density is employed. A possible explanation of this apparent inconsistency is to ascribe a mild degree of passivity to gallium—an explanation in keeping with the fact that pure gallium precipitates copper only very slowly from its solutions. After preliminary purification by electrolysis, which easily eliminates indium and many other metals, pure gallium was freed from zinc by ignition in a high vacuum or by crystallisation, giving material of constant melting point. The melting point on the international hydrogen scale is 29·75°. The purest material has D 5·904 for the solid and D 6·095 for the liquid, both at the melting point. The expansion 0·00531 c.c. per gram on solidification is shown not to be due to impurities. The compressibility of solid gallium at 20° is 0·0000020 and that of the liquid about twice as great. The coefficient of cubical expansion of solid gallium is 0·000055. Hence $D^{20} = 5·907$ and its atomic volume 11·85. The surface tension of liquid gallium in carbon dioxide at 30° is 36·54 mg./mm. The latent heat of fusion, calculated by the Clapeyron formula and the change of the melting point with pressure, was found to be 19·04 cal. per gram at 173 megabars pressure, that is, the melting point is lowered 0·00207° by an increase in pressure of one atmosphere. J. F. S.

Separation of Gallium from Indium and Zinc by Fractional Crystallisation of the Cæsium Gallium Alum. PHILIP E. BROWNING and LYMAN E. PORTER (*J. Amer. Chem. Soc.*, 1921, **43**, 126).—Fractionation of a solution of a mixture of gallium and indium cæsium alums containing gallium and indium in the ratio $Ga_2O_3 : In_2O_3 = 26·5 : 73·5$ gave a first crop of crystals containing the oxide in the ratio $Ga_2O_3 : In_2O_3 = 14·9 : 85·1$. After five fractions had been obtained it was found that the first consisted entirely of gallium, whilst the fifth contained the two oxides in the ratio $Ga_2O_3 : In_2O_3 = 0·6 : 99·4$. Recrystallisation of a mixture of zinc sulphate and gallium cæsium alum of the composition 2 grams of ZnO and 1·0 gram of cæsium gallium alum gave on the first recrystallisation crystals containing $Ga_2O_3 : ZnO = 98 : 2$, and after the second recrystallisation no zinc could be detected. J. F. S.

Reduction by Metals in Acid Solutions. I. The Reduction of Acid Ferric Sulphate Solutions by Zinc and Magnesium. SAMUEL SUGDEN (T., 1921, **119**, 233—238).

System and Constitution of Derivatives of Molybdic Acid. II. L. FORSÉN (*Compt. rend.*, 1921, **172**, 327—330. Compare this vol., ii, 205).—The author considers that the most probable formula for metamolybdic acid is $[Mo_{12}O_{42}H_6]H_6$, and gives for it a constitutional formula showing it as a product of condensation of four molecules of molybdic acid (*loc. cit.*). He has converted molybdic acid into metamolybdic acid by warming it with hydrochloric acid and a little nitric acid. W. G.

Identity of Trechmann's "β-Tin" with Stannous Sulphide. L. J. SPENCER (*Min. Mag.*, 1921, **19**, 113—123).—A re-examination of the original material described by C. O. Trechmann in 1879 (A., 1882, 576) as an orthorhombic modification of tin proves that he made his crystallographic determinations on crystals of one kind (namely, stannous sulphide), whilst the chemical analysis was made on crystals of another kind (namely, metallic tin). Tin is therefore dimorphous, and not trimorphous, "white tin" being tetragonal and "grey tin" cubic. Orthorhombic crystals ($a : b : c = 0{\cdot}3874 : 1 : 0{\cdot}3558$, Trechmann) of stannous sulphide, SnS, are produced, under certain conditions, in considerable quantity during the process of tin smelting. The material has the form of thin, flexible plates and scales with an iron-black colour and metallic lustre, somewhat resembling graphite in appearance and hardness (H 2). It dissolves in hydrochloric acid with evolution of hydrogen sulphide. Analysis of material from which globules of tin and needles of iron stannide could not be separated gave: Sn 81·48, Fe 1·70, S 15·14, insoluble 0·90, total 99·22, D 5·52, corresponding with SnS 72·2, Sn 15·0, $FeSn_3$ 12·8%, and re-calculated D for the SnS 5·0 (previous determinations range from 4·852 to 6·557). The associated tetragonal needles of iron stannide are tin-white with brilliant metallic lustre, brittle, and non-magnetic. They dissolve in hydrochloric acid with evolution of hydrogen. Analysis gave Sn 84·94, Fe 13·48, S 0·24, total 98·66, D 7·77, corresponding with $FeSn_3$. Rhombohedral tin arsenide, Sn_3As_2 (Sn 70·22—70·62, As 29·78—29·38%) was prepared by J. E. Stead by slowly cooling an alloy containing Sn 95, As 5%; the crystals ($a : c = 1 : 1{\cdot}2538$) have the form of thin graphite-like scales. L. J. S.

Preparation of Insoluble Thorium Compounds [Double Metaphosphate and Sulphate of Thorium]. LINDSAY LIGHT Co., Brit. Pat., 156892).—A double metaphosphate and sulphate of thorium, $Th(PO_3)_2SO_4$, of the same composition but purer than the compound obtained by heating with sulphuric acid at a high temperature a natural mineral containing thorium and phosphates such as monazite sand (cf. U.S. Pat., 1323735), is prepared in the form of white, acicular crystals by dissolving 120 grams of thorium sulphate, $Th(SO_4)_2,8H_2O$, in 50 c.c. of 80% phosphoric acid, and heating for ten hours at 280°. Water and sulphuric acid fumes are evolved and the product forms a nearly solid, crystalline mass, insoluble in water or in dilute acids. The same substance is also obtained by heating thorium phosphate with an equal weight of sulphuric acid, preferably in presence of 20—40% of phosphoric acid, for ten hours at a temperature above 260°. G. F. M.

Preparation of Spongy Platinum. R. FEULGEN (*Ber.*, 1921, **54**, [*B*], 360—361).—The following method yields a material which does not tend to pass into colloidal solution during the process of washing and before removal of the chloride is complete.

A solution of chloroplatinic acid (5 grams) in water (5 c.c.) is mixed with formaldehyde solution (40%, 7 c.c.), and sodium

hydroxide (5 grams) dissolved in water (10 c.c.) is gradually added. The mixture is allowed to remain for half an hour at the ordinary temperature, then heated for fifteen minutes at 55° and poured into a half-litre flask half full of water. The flask is agitated violently for a few minutes, which causes the precipitate to settle in coarse particles leaving an almost colourless supernatant liquor. The latter is decanted and the precipitate is washed with water strongly acidified with acetic acid, which again causes the formation of coarse particles which can now be washed as requisite without showing any tendency to pass into the colloidal state. The metal is finally filtered and dried in a vacuum over sulphuric acid. Great caution must be observed in the subsequent admission of air into the desiccator as the metal readily becomes incandescent owing to absorption of oxygen. Previous to use, it is advisable to grind and wash it once more. A very active catalyst is thus obtained.

H. W.

Action of Hydrochloric Acid on the Tetroxides of Osmium and Ruthenium. HEINRICH REMY (*J. pr. Chem.*, 1920, [ii], **101**, 341—352).—The contradiction between the observation of Milbauer (A., 1918, ii, 202) that osmium tetroxide is decomposed by concentrated hydrochloric acid at the ordinary temperature, and that of Ruff and Mugdan (A., 1919, ii, 108) that no action occurs, is due to differences in the strengths of acid employed. Acid with D>1·160 reacts at the ordinary temperature, giving osmium tetrachloride (compare Milbauer, *loc. cit.*); ruthenium tetroxide reacts still more easily (compare Ruff and Mugdan, *loc. cit.*), forming the trichloride.

J. K.

Mineralogical Chemistry.

A New Variety of Antimoniferous Bismuth Sulphide. S. PIÑA DE RÚBIES (*Anal. Fís. Quím.*, 1920, **18**, 335—338).—An antimoniferous variety of bismuth sulpho-telluride has been found associated with oruetite (A., 1919, ii, 235). The minerals are almost identical in appearance, colour, etc., but differ slightly in hardness. The new variety has D 6·8, whilst oruetite has D 7·8. As a criterion for the separation of fragments of the two varieties, electrical conductivity has been used. The composition of the new variety is as follows:

Bi.	Sb.	Pb.	Sn.	S.	Te-Se.	Cu.	As.
73·38	4·50	0·82	0·09	17·08	4·98	trace	trace

The composition corresponds with the formula

$$8Bi_2S_3,Sb_2S_3,Bi_2(Se,Te)_3.$$

G. W. R.

Minerals from Slata, Tunis. H. BUTTGENBACH (*Bull. Soc. franç. Min.*, 1920, **43**, 24—67).—A crystallographic description of fine crystals of cerussite, anglesite, etc. Colourless crystals of calcite enclose brown filaments, which, as shown by the following analysis, consist of a hydroxide of iron and aluminium with the composition $3Al_2O_3,3Fe_2O_3,2H_2O$:

CaO.	Fe_2O_3.	Al_2O_3.	H_2O.	CO_2.	Total.
53·44	2·54	1·58	0·38	42·02	99·96

L. J. S.

Sarcopside from New Hampshire. EDW. F. HOLDEN (*Amer. Min.*, 1920, **5**, 99—102, 166).—This mineral (M. Websky, 1868) has sometimes been regarded as altered triplite. It is, however, probably a distinct species, as shown by an exmination of fresh material found in pegmatite at Deering, New Hampshire. This forms irregular slabs with fibrous structure and silky lustre. The colour is flesh-red to lavender, but soon alters on exposure to blue, green, or brown; the streak is pale straw-yellow. D 3·64, H 4, n 1·725. Analysis gave :

Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	P_2O_5.	F.	H_2O.	Insol.	Total less O for F.
1·70	39·87	10·83	4·38	0·68	33·26	4·35	1·53	3·22	97·99

Neglecting water (which is expelled below 110°) and calculating all the iron as ferrous, this gives the formula $2R_3P_2O_8,RF_2$ or $R_7F_2(PO_4)_4$, in which the ratios lie between those of triplite and apatite. Griphite is perhaps an impure form of sarcopside.

L. J. S.

Trigonite and Dixenite, Two New Minerals from Långban, Sweden. GUST. FLINK (*Geol. För. Förh.*, 1920, **42**, 436—452).—Trigonite is found together with native lead in crevices in dolomite. The crystals are monoclinic with domatic hemihedrism (clinohedral class), and have the form of triangular wedges;

$$a : b : c = 1{\cdot}07395 : 1 : 1{\cdot}65897,\ \beta = 91^\circ\ 31'.$$

They are sub-transparent with sulphur-yellow colour and vitreous to adamantine lustre. D 8·28, H 2—3; refractive indices α 2·08, γ 2·16. Easily soluble in dilute nitric acid. Analysis I, by R. Mauzelius, gives the formula $Pb_3MnH(AsO_3)_3$.

	As_2O_3.	SiO_2.	PbO.	FeO.	MnO.	CaO.	MgO.	H_2O.	Insol.	Total.
I.	28·83	—	63·40	0·15	6·79	0·23	0·11	0·81	0·13	100·45
II.	30·55	8·66	—	4·54	48·94	0·28	0·50	3·38	—	100·32*

Dixenite forms aggregates of thin folia in crevices of fine-grained hæmatite or in dolomite. It is black and sub-translucent with resinous to metallic lustre; by transmitted light a glowing red; optically uniaxial and positive. X-ray photographs show it to be rhombohedral or hexagonal. D 4·20, H 3—4, mean refractive index 1·96. Easily soluble in hydrochloric acid with separation of part of the silica. Analysis II, by R. Mauzelius, gives the formula $(MnOH)_2Mn_3SiO_3(AsO_3)_2$ or $MnSiO_3 + 2(MnOH)MnAsO_3$.

L. J. S.

* Including P_2O_5 0·09, CuO 3·38.

Armangite, a new Arsenite from Långban, Sweden. G. AMINOFF and R. MAUZELIUS (*Geol. För. Förh.*, 1920, **42**, 301—309).—The mineral occurs in calcite veins with barytes, fluorite, hæmatite, etc. Crystals are rhombohedral ($a : c = 1 : 1{\cdot}3116$); H 4, D 4·23. Colour black, streak brown, thin slices brown to yellow; optically uniaxial and negative; refractive indices high ($>1{\cdot}79, <1{\cdot}93$). Analysis by R. Mauzelius gave:

As_2O_3.	Sb_2O_3.	PbO.	FeO.	MnO.	CaO.	MgO.	H_2O.	CO_2.	Insol.	Total.
42·92	0·40	0·32	2·19	45·06	2·83	0·49	0·71	5·08	0·20	100·20

The mineral dissolves readily in hydrochloric acid with separation of arsenic trioxide. An attempt was made to determine the degree of oxidation of the arsenic. The carbon dioxide appears to be always present as admixed carbonates (of manganese, calcium, and magnesium, amounting to 12%); deducting these and limonite, the formula is that of an ortho-arsenite, $Mn_3(AsO_3)_2$. Only two mineral arsenites, ecdemite and trippkeite, have previously been known. L. J. S.

Pitchblende, Monazite, etc., from Bengal. G. H. TIPPER (*Rec. Geol. Surv. India*, 1919, **50**, 255—262).—These minerals are found, together with torbernite, autunite, apatite, and columbite, in pegmatite near the village of Pichhli in the Gaya district. The pitchblende (anal. I) forms the core of pale yellow, soft, and friable nodules of uranium-ochre (anal. II); cubo-octahedra of uranium-ochre pseudomorphous after pitchblende are also found. The following partial analyses indicate the nature of the change. Both minerals when dissolved in nitric acid evolve much gas.

	SiO_2.	U_3O_8.	Rare-earths, including Th.	PbO.	$\underbrace{\text{Fe. Mn. Ba.}}$	P_2O_5.	Sp. gr.
I.	1·16	66·24	13·9	12·49	n.d.	—	6·68
II.	12·09	34·74	23·16	19·1	n.d.	n.d.	—

Monazite as large crystals and crystalline masses (up to $1\frac{1}{2}$ kilos) has D 5·2 and contains ThO_2 9·95%. Columbite crystals weigh up to 6 kilos; D 5·28—5·52. L. J. S.

Japanese Minerals containing Rare Elements. I. Analysis of Naegite, Fergusonite, and Monazite, from Naegi, Mino Province. YÛJI SHIBATA and KENJIRÔ KIMURA (*J. Chem. Soc. Japan*, 1921, **42**, 1—16).—Naegite gave on analysis:

ZrO_2.	SiO_2.	$(Nb,Ta)_2O_5$.	ThO_2.	Rare earths.	UO_2.	Fe_2O_3.
53·03	29·55	1·12	2·85	6·68	2·69	1·42

H_2O $<110°$.	H_2O $>110°$.	Total.
0·72	2·05	100·11

The following rare earths were detected spectroscopically: Ce, Nd, La, Pr, Sm; Y, Dy, Er, Yb, Gd, Tb, and Ho.

Fergusonite gave on analysis:

SiO_2.	$(Nb,Ta)_2O_5$.	TiO_2.	ThO_2.	CeO_2.	Nd_2O_3, etc.	Y_2O_3, etc.
2·83	43·77	1·65	2·91	1·26	1·99	37·64

UO_2.	Fe_2O_3.	Al_2O_3.	CaO.	H_2O $<110°$.	H_2O $>110°$.	Total.
0·85	3·97	0·20	1·16	0·24	1·85	100·32

Spectroscopic evidence was obtained of the presence of the following rare earths: Ce, Nd, Sm, La; Y, Dy, Er, Yb, and Gd.

The sample of monazite sand contained P_2O_5 20·42%, SiO_2 10·81%, ThO_2 8·52%, Ce_2O_3 19·44%, Nd_2O_3 etc., 19·70% Dy_2O_3 etc. 3·54%. $H_2O < 110°$ 0·69%, $H_2O > 110°$ 1·64%. Traces of TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2, Al_2O_3, Fe_2O_3, CaO, and MgO, etc., were not estimated. The presence of the following rare earths, Ce, Nd, La, Sm, Pr; Dy, Yb, Gd, Er, Eu, Tb, Y, Ho, Tu, and Ru, was shown spectroscopically. K. K.

Plazolite, a New Mineral. WILLIAM F. FOSHAG (*Amer. Min.*, 1920, **5**, 183—185).—This occurs in the metamorphic limestone at Crestmore, California (A., 1919, ii, **113**), as small, colourless rhombic dodecahedra embedded in an undetermined foliated white mineral. It is brittle with conchoidal fracture and glassy lustre; D 3·129, H $6\frac{1}{2}$, n 1·710. It is easily soluble in hydrochloric acid. The powdered mineral has a slightly alkaline reaction, but strong after ignition. At 150° the loss is only 0·21%. Analyses I–III give the formula $3CaO,Al_2O_3,2(SiO_2,CO_2),2H_2O$, in which carbon dioxide is assumed to replace silica. The high ratio of bases requires a complex grouping to satisfy an orthosilicate formula. The mineral appears to be most nearly related to sodalite.

	SiO_2.	Al_2O_3.	CaO.	MgO.	H_2O.	CO_2.	Total.
I.	24·13	23·66	40·22	0·12	12·21		100·34
II.	23·85	22·77	40·13	—	9·39	3·41	99·55
III.	25·06	24·63	40·13	trace	9·04	1·13	99·99

L. J. S.

Analytical Chemistry.

The Indicator Properties of Two New Phthaleins (1 : 2 : 3-Xylenolphthalein and ortho-α-Naphtholphthalein). WILHELM CSÁNYI (*Zeitsch. Elektrochem.*, 1921, **27**, 64—68).—The phthalein from 1 : 2 : 3-xylenol and phthalic anhydride is a valuable indicator, the change from colourless to blue being completed within the range of hydrogen-ion concentrations p_H 8·9 and 10·2. It has the advantage that the colour is unaffected by excess of alkali or by alcohol. Ortho-α-naphtholphthalein shows a colour change at about the same hydrogen-ion concentration, but as the colour change is less sharp, the substance is but slightly soluble in water and alcohol, and the colour is discharged by excess of alkali; it is less valuable as an indicator than the xylenolphthalein. E. H. R.

Separating Funnel for Quantitative Extractions. R. LUTHER (*Zeitsch. angew. Chem.*, 1921, **34**, 66—67).—The stem of the tap is not placed directly below the lower part of the funnel, and the bore of the tap is inclined to connect these two parts; a half-turn of the tap cuts off the funnel from the stem and at

the same time connects the latter with a small funnel open to the air; any liquid retained in the stem is thus discharged, and, if required, the stem may be washed out by introducing water or other liquid into the small funnel. W. P. S.

A Probable Error in Estimations by means of the Hydrogen Electrode. C. LOVATT EVANS (*J. Physiol.*, 1921, **54**, 353—366).—Electrometric measurements of the reaction of the blood or bicarbonate solutions yield results which represent H-ion concentrations about 60% higher (P_H 0·2 lower) than those given by the colorimetric method of Dale and Evans (this vol., i, 142). The latter values are regarded as correct, and agree with calculations based on the apparent dissociation constant of carbonic acid (k) and the degree of ionisation of bicarbonate (δ) as determined by conductivity measurements (Walker and Cormack, T., 1900, **77**, 13). When constants (k or δ) derived from hydrogen electrode measurements are used in calculating the P_H of bicarbonate solutions, the results naturally agree with those of direct observation by means of the hydrogen electrode, because in such a calculation k is larger or δ smaller than is found by the conductivity method. Such calculated results obviously do not agree with colorimetric determinations. A source of error in the hydrogen electrode lies in the catalytic production of formic acid, when the solution in the hydrogen electrode contains carbonates. G. B.

A Simple Apparatus for the Identification of Gases Evolved in the Qualitative Tests for Acids. EUGÈNE LUDWIG (*Bul. Soc. Chim. România*, 1920, **2**, 20—23).—The apparatus consists essentially of a small reaction flask, fitted with a cork carrying a safety thistle funnel, the two bulbs of which are joined by a capillary tube in which the suitable reagent for detecting the particular gas expected is placed. Only a very small amount of reagent is required, and hence a trace of a gas may be detected. W. G.

Microchemical Analysis with Reagents Sensitised by Saturation. EUGÈNE LUDWIG (*Bul. Soc. Chim. România*, 1920, **2**, 28—32).—The reagent to be used is saturated with a salt containing the ion which is to be detected, the formation of a precipitate being observed under a microscope. Thus $N/2$-silver nitrate saturated with sodium sulphate may be used for the detection of sulphates; a solution of potassium pyroantimonate saturated with sodium chloride for the detection of sodium, and a solution of platinic chloride saturated with potassium chloride for the detection of potassium. W. G.

Microchemical Analysis with Reagents Sensitised by Saturation. EUGÈNE LUDWIG and D. BUTESCU (*Bul. Soc. Chim. România*, 1920, **2**, 32—35. Compare preceding abstract).—The reagents recommended are, $N/2$-silver nitrate treated with sodium acetate until a precipitate just appears, for the detection of acetates; a solution of uranyl acetate saturated with a sodium

salt for the detection of sodium. For the identification of borax a $N/2$-solution of silver nitrate is recommended. On the addition of a few particles of borax to this solution very small crystals appear, and on warming the slide gently the undissolved particles become black. W. G.

Action of Iodine in the Cold on Different Metals. Detection of the Presence of Chlorine in the Atmosphere. CAMILLE MATIGNON (*Compt. rend.*, 1921, **172**, 532—534).—Iodine placed on thin sheets of metals such as silver, copper, aluminium, tin, or zinc gradually converts the whole of the metal into the iodide at the ordinary temperature, the velocity of the reaction varying with the metal. This change may be adapted for the detection of chlorine in the atmosphere. A thin sheet of beaten silver 1 cm. in diameter, forming part of an electric circuit, is covered with damp potassium iodide and exposed to the air. Any chlorine in the air decomposes the potassium iodide, and the iodine liberated speedily converts the silver into silver iodide and the electric circuit is thus broken, and by a suitable arrangement an audible warning may be given. W. G.

A Method for the Estimation of Chlorides in Small Quantities of Liquids. STEFAN RUSZNYÁK (*Biochem. Zeitsch.*, 1921, **114**, 23—26).—The application of Korányi's method as a micromethod for the estimation of chlorides is described. Exact results are obtained by this method. S. S. Z.

Estimation of Chlorides in Trichloroacetic Acid Filtrates from Whole Blood and Plasma. MILLARD SMITH (*J. Biol. Chem.*, 1921, **45**, 437—447).—The use of trichloroacetic acid as a precipitant for proteins in blood and plasma does not interfere with the estimation of chlorides. Certain modifications of the process are given. J. C. D.

A System of Blood Analysis. II. Simplified Method for the Estimation of Chlorides in Blood or Plasma. J. C. WHITEHORN (*J. Biol. Chem.*, 1921, **45**, 449—460).—Proteins are removed by the reagents employed by Folin and Wu in their system of blood analysis (A., 1919, ii, 308). Chlorides are estimated in the protein-free filtrate by a modified Volhard method. J. C. D.

The Estimation of Chlorides in Blood Plasma. J. HAROLD AUSTIN and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1921, **45**, 461—463).—It is advisable to remove proteins by a preliminary precipitation before making the estimation of chlorides. J. C. D.

Estimation of Chlorine in Solid Tissues. RICHARD D. BELL and EDWARD A. DOISY (*J. Biol. Chem.*, 1921, **45**, 427—435).—The sample of tissue is decomposed in a small digestion tube by heating with strong sulphuric acid and ammonium or potassium

persulphate, a small globule of mercury being added to act as a catalyst. The gases formed during the incinceration are drawn by a current of air into absorption tubes containing sodium carbonate.

After the digestion is completed the liquid in the absorption tubes is transferred quantitatively to a 150 c.c. Erlenmeyer flask, neutralised with sulphuric acid, using methyl-orange as indicator, and the carbon dioxide and sulphur dioxide are expelled by boiling. The chlorine present as chloride is then estimated by one of the usual methods. J. C. D.

A New Method for the Detection of Chlorine and Bromine Ions in the Presence of Iodine Ions. EUGENE LUDWIG (*Bul. Soc. Chim. România*, 1920, **2**, 23—28).—The halogens are precipitated with silver nitrate in boiling acid solution, the precipitate being collected and washed till free from silver nitrate. A portion is then boiled with as small an amount as possible of *N*/10-ammonium hydroxide solution. If the solution so obtained becomes turbid on the addition of a trace of a soluble chloride, chlorine ions were originally present. A somewhat more delicate test is to add one drop of a concentrated solution of sodium bromide. If the liquid remains clear, chlorine and bromine ions were originally absent. A slight turbidity at this stage may be due to bromine ions or a trace of chlorine ions originally present, and to confirm the presence or absence of bromides another portion of the silver haloid precipitate is boiled with *N*-ammonia, and the solution obtained is treated with zinc and an excess of sulphuric acid and warmed. When the action is completed the liquid is decanted and tested for bromine by the addiiion of chlorine water in the presence of chloroform in the usual manner. W. G.

A New Method for the Estimation of Bromine in very small Quantities. ERNST OPPENHEIMER (*Arch. Expt. Path. Pharm.*, 1921, **89**, 17—28).—Schiff's reagent is coloured deep blue violet by bromine. On the addition of chlorine water to such a solution when acidified with sulphuric acid it becomes intensively violet, greyish-violet, and eventually, when there is an excess of chlorine, golden-yellow. These colorations are utilised by the author for the estimation of small quantities of bromine. S. S. Z.

Electro-titration of Hydriodic Acid and its use as a Standard in Oxidimetry. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1921, **43**, 14—23).—Solutions of iodides in dilute sulphuric acid may be accurately titrated electrometrically with potassium permanganate. The reaction is carried out in a bottle with three necks, through one the end of the burette passes; a narrow tube by which air or carbon dioxide is passed enters by the second neck, and the third carries a bright platinum electrode and the connecting tube of a calomel electrode. The gas is passed in simply for the purpose of stirring the solution. The *E.M.F.* of the system is determined as the titration proceeds, and the point

where a sudden increase occurs is the end point of the reaction. The reaction is affected by the presence of chlorides or bromides, but may be carried out if the amount of chloride does not exceed that of the iodide, and if the bromide concentration does not exceed a quarter of that of the chloride. Dichromate and iodate as oxidisers in $0{\cdot}02N$ and $0{\cdot}05N$ solutions may be accurately titrated by adding solutions of either to a measured excess of an iodide in sulphuric acid solution, and titrating the excess of iodide with permanganate as described above. Silver has been estimated in the same way. It is shown that the high results obtained by Crotogino in titrating iodide with permanganate were not due to the formation of iodic acid before the end point was reached (A., 1900, ii, 685). Using this method, potassium dichromate shows its theoretical oxidising power. J. F. S.

Volumetric Estimation of Polysulphide-sulphur. A. Wöber (*Zeitsch. angew. Chem.*, 1921, **34**, 73).—A measured quantity of the polysulphide solution, diluted previously with boiled water, is added to an excess of 10% sodium sulphite solution and the mixture is heated at 50° until colourless; the polysulphide reacts with the sulphite, yielding thiosulphate. After fifteen minutes, the solution is diluted to a definite volume and the thiosulphate is estimated in an aliquot portion by Bodnár's method (A., 1915, ii, 161, 629). If the polysulphide already contains thiosulphate, this must be estimated previously and an allowance made for its quantity. When the polysulphide contains alkali carbonate, it must be treated with cadmium acetate or zinc sulphate before the thiosulphate is estimated. W. P. S.

Estimation of Nitric Acid. L. W. Winkler (*Zeitsch. angew. Chem.*, 1921, **34**, 46).—In the estimation of nitric acid as nitron nitrate (cf. Treadwell's handbook), acetic acid (1 c.c. of the glacial acid per 100 c.c. of neutral solution) is preferable to sulphuric acid for acidifying the original solution. Cooling to 0° may be avoided by keeping the reaction mixture for twenty-four hours in the dark at 15—20°. The precipitate may be collected on a small felt of cotton wool in a cup-shaped filter, instead of on a Gooch crucible. The 10 c.c. of ice-cold water prescribed by Treadwell for washing is quite insufficient; 50 c.c. of a saturated solution of nitron nitrate at the ordinary temperature may be used, the last washing being removed as completely as possible by suction. The accuracy of the method is not affected by the presence of sulphates or iodates, but chlorides lead to high results which may be corrected by reference to a table. J. H. L.

A Short Test for Easily Soluble Phosphate in Soils. O. M. Shedd (*So l Sci.*, 1921, **11**, 111—122).—In the first part of the paper a preliminary account is given of some work on the reaction between dilute acids and the phosphorus compounds of the soil, the results of which agree fairly well with those of Russell and Prescott (*J. Agric. Sci.*, 1916, **8**, 6).

The test described consists in shaking 10 grams of air-dried soil with 25 c.c. of $N/5$-nitric acid for five minutes, filtering the solution and adding to the filtrate, collected in a standard size test-tube, 1 or 2 c.c. of a 60% solution of ammonium nitrate and 5 c.c. of ammonium molybdate solution. The contents of the tube are heated at 60°, shaken several times and allowed to remain. The volume of the precipitate is judged by the eye and the soluble phosphate in the soil classed as "large," "fair," "moderate," "very moderate," etc., in decreasing order of precipitate obtained. This classification of different soils is in agreement with that obtained by digesting the soils for five hours with larger amounts of nitric acid and determining the extracted phosphate quantitatively. Any soil classed as very moderate to moderate or under, that is, containing 0·005—0·0075% or less of soluble phosphorus, will probably respond to applications of phosphatic fertilisers.

W. G.

Estimation of Citric-soluble Phosphate in Superphosphate. P. MÜLLER (*Chem. Zeit.*, 1921, **45**, 178).—In the estimation of citric-soluble phosphate, complete precipitation of the magnesium ammonium phosphate is not secured by shaking for half an hour; the precipitate must be left over night before filtering. Comparative estimations made directly after shaking, and after keeping, indicated that in the former case the results are too low, the average difference for seven tests being 0·44%. The slowness of precipitation is probably due to the presence of other salts. W. J. W.

Detection of Arsenic. L. W. WINKLER (*Pharm. Zentr.-h.*, 1921, **62**, 125—128).—Bettendorf's reagent (stannous chloride in hydrochloric acid solution) will detect 0·01 mg. of arsenic trioxide in 2 c.c. of solution; the presence of sulphuric acid does not interfere. In testing dark coloured solutions, the latter should be treated with zinc and sulphuric acid, the evolved gases passed through hydrochloric acid, and the latter then tested with the reagent. The evolved gases may also be passed through Nessler reagent; a precipitate is obtained if arsenic is present, but antimony, phosphorus, and sulphur compounds yield a similar reaction. A test, similar to the Gutzeit test, is described, the arsenic being detected by means of filter paper moistened with gold chloride.

W. P. S.

The Estimation of Arsenic in Organic Compounds. GEORGE ROSS ROBERTSON (*J. Amer. Chem. Soc.*, 1921, **43**, 182—185).—The compound is oxidised with a mixture of nitric and sulphuric acids (compare Morgan, "Organic Compounds of Arsenic and Antimony," 1918, 349), the liquid is freed from nitrous compounds by means of ammonium sulphate, and the arsenic estimated by the method of Gooch and Morris (A., 1900, ii, 686). The results by this rapid method are quite comparable with those from the Carius method. W. G.

Sensitive Test for the Hydrides of Arsenic, Antimony, and Phosphorus by Means of Gold Chloride. WALTHER ZIMMERMANN (*Apoth. Zeit.*, 1921, **36**, 26; from *Chem. Zentr.*, 1921, ii, 431).—Basing his experiments on Lehbert's observation that gold chloride is reduced by arsenic trihydride, the author has shown that a drop of sodium aurichloride solution spread on a piece of filter paper is scarcely affected by pure hydrogen, but is coloured violet by small amounts of the hydrides of arsenic, antimony, or phosphorus. A distinct coloration was obtained with 0·00284 mg. As in liquor kali arsenicosi in two minutes, and a recognisable reaction with 0·00015 mg. As in salvarsan in ten minutes; distinct and slight reactions were observed with 0·00124 mg. Sb in potassium antimonyl tartrate in five minutes, and with 0·25 mg. P in calcium hypophosphorosum respectively. Organic matter must be destroyed; hydrogen sulphide interferes with the reaction by giving a brown coloration. H. W.

Criticism of the Methods of Estimating Small Amounts of Carbon Monoxide in Air and in Flue Gases. DANIEL FLORENTIN and H. VANDENBERGHE (*Compt. rend.*, 1921, **172**, 391—393).—The two methods considered are Gautier's method, in which the carbon monoxide is oxidised by iodic anhydride (A., 1898, ii, 537) and the method of Ogier and Kohn-Abrest (A., 1908, ii, 631, 632) depending on the formation of carboxyhæmoglobin. The first method is open to the objection that other gases, not easy to remove, may be present, which also oxidise iodic anhydride. Certain manipulative precautions are indicated, and the authors do not apparently favour this method. They obtained concordant results by the second method, but advise each analyst to prepare his own scale. If the air or gas to be analysed contains more than 1 part of carbon monoxide per 1000 it should be first diluted before being passed through the hæmoglobin solution. W. G.

Simplified Methods of Analysis in the Calcium Group. EUGÈNE LUDWIG and (MLLE) HÉLÈNE SPIRESCU (*Bul. Soc. chim. România*, 1920, **2**, 35—37).—Strontium is in every case detected by the flame test. By precipitation of the metals of this group with ammonium carbonate in the presence of ammonium chloride, the filtrate will in every case contain sufficient calcium and barium, if these elements are present, to permit of their detection with ammonium oxalate and sulphuric acid respectively. Alternatively, ammonium oxalate is used as the group precipitant. The filtrate will then contain sufficient barium for its detection with sulphuric acid, and calcium may be detected microchemically in the precipitate by treatment with sulphuric acid (Behrens-Kley, *Microchemische Analyse*, 1915). W. G.

Importance of Adsorption in Analytical Chemistry. VI. Adsorption of Lead and Copper by Filter-paper. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 152—159. Compare this vol., ii, 213).—Lead is not completely adsorbed from its solutions

by filter-papers with low ash-alkalinity. If, however, the solution is treated with sodium hydroxide solution containing carbonate, most of the lead is precipitated and the remainder absorbed, and on subsequently treating the filter with acetic acid, all the lead is re-dissolved. This method may be applied to the estimation of lead in drinking water, but a preliminary blank test for lead in the filter paper must be made. For the quantitative estimation, the lead in the solution, before and after adsorption, is precipitated as sulphite and collected on asbestos. The precipitate is then oxidised with bromine, and excess of the latter determined iodometrically. With high concentrations, adsorption is proportional to the alkalinity of the filter ash, and to remove lead entirely from its solutions by means of filter-paper or cotton wool, these must have a high alkalinity; no appreciable quantities of lead are adsorbed when the ash-alkalinity is negligible.

Adsorption of copper by filter-paper is very slight, and bears no relation to the alkalinity of the ash. From solutions in distilled water, more copper is adsorbed than from solutions to which sodium carbonate or ammonia is added. From dilute ammoniacal solutions of copper more is adsorbed than from those of higher concentration. In contradistinction to that of lead, the adsorption of copper from neutral solutions is negligible, but from solutions in ammonia a high adsorption takes place. W. J. W.

The Importance of Adsorption in Analytical Chemistry. VII. The Adsorption of Silver, Mercury, and Other Metals. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 233—241).—The taking up of heavy metals from solutions of their salts by cotton-wool and filter paper is not a physical adsorption, but is a result of chemical action with the ash of the cellulose, which functions as a permutite in which the bivalent anion may be replaced by hydrion or a heavy metal ion. Pure ash-free cellulose would probably not take up metals at all. The quantities fixed by ordinary ash-containing cellulose may be much reduced by addition of acid to the solutions. S. I. L.

Use of Gallium Ferrocyanide in Analysis. LYMAN E. PORTER and PHILIP E. BROWNING (*J. Amer. Chem. Soc.*, 1921, **43**, 111—114).—Gallium ferrocyanide may be filtered by suction if a pad made of shredded filter-paper is placed on top of a double filter-paper and the suction employed is gentle. The precipitate after washing is ignited and weighed as the mixed oxides of gallium and iron. Gallium may be recovered from the ferrocyanide by treating with sodium hydroxide, whereby the whole passes into solution as sodium ferrocyanide and an alkali salt of gallium, and then treating with carbon dioxide, which precipitates the gallium as hydroxide. An alternative method consists in treating the alkaline solution of gallium ferrocyanide with hydrogen peroxide to oxidise the sodium ferrocyanide to sodium ferricyanide, and then boiling with ammonium chloride, when pure gallium hydroxide is precipitated. When zinc is present neither of the above methods

is available. In this case the metals are precipitated together as ferrocyanides which are dissolved in sodium hydroxide, and the hydroxide precipitated by carbon dioxide. The hydroxides are dissolved in hydrochloric acid, and the gallium precipitated by boiling with ammonium hydrogen sulphite. Alternatively, the alkaline solution of the ferrocyanides is treated with hydrogen sulphide, which precipitates the zinc, the gallium then being obtained by either of the methods described above. J. F. S.

Reaction of Manganese Salts. V. MACRI (*Ann. Chim. anal.*, 1921, [ii], **3**, 55—56).—The author has described previously (A., 1917, ii, 511) the oxalate reaction for manganese as given by Caron and Raquet (A., 1919, ii, 351) and by Denigès (A., 1920, ii, 558). W. P. S.

The Interference of Phosphates in the Detection of Manganese and its Avoidance. TH. SABALITSCHKA and H. NIESEMANN (*Ber. deut. Pharm. Ges.*, 1921, **31**, 30—36. Compare A., 1921, ii, 134).—The failure to detect manganese in presence of an excess of barium or strontium phosphate, when the separation of phosphoric acid is conducted according to Schmidt's analytical scheme, is obviated by the following procedure: The precipitate obtained with ammonium sulphide is dissolved in 5% hydrochloric acid and filtered from insoluble nickel and cobalt sulphides. The solution is then evaporated with 2—3 grams of concentrated sulphuric acid and a like quantity of saturated potassium sulphate solution until white fumes are evolved, any ferrous iron being previously oxidised by nitric acid. The mixed sulphates obtained are extracted with alcohol to remove sulphuric and phosphoric acids (small quantities of manganese and zinc sulphates and most of the chromium also pass into solution). The residue insoluble in alcohol is extracted with dilute hydrochloric acid and the insoluble sulphates of barium, strontium, and calcium are filtered off. From the filtrate iron, aluminum, and chronium are precipitated with ammonia, and then the sulphides of zinc and manganese with ammonium sulphide. The final filtrate contains calcium and magnesium. G. F. M.

The Sodium Acetate Method for the Separation of the Bivalent Metals from the Tervalent Metals in the Ammonium Sulphide Group. TH. SABALITSCHKA (*Ber. deut. Pharm. Ges.*, 1921, **31**, 36—37. The sodium acetate method described by Macri (A., 1920, ii, 699) for the separation of iron, aluminium, and chromium from zinc, manganese, etc., is useless in presence of chromium, as this metal is not precipitated at all when alone, and only partly in the presence of iron or aluminium. G. F. M.

Use of Spot Reactions in Qualitative Analysis. FRIEDRICH FEIGL and ROSA STERN (*Zeitsch. anal. Chem.*, 1921, **60**, 1—43). —A description of the application of spot reactions on filter-paper

to the detection of numerous substances, especially in mixtures. Special mention is made of the reactions of aluminium, uranium, and chromium with alizarin colouring matters, and of manganese with benzidine. W. P. S.

Estimation of Small Quantities of Chromium in Steels. B. S. Evans (*Analyst*, 1921, **46**, 38—42).—Four grams of the sample are dissolved in 30 c.c. of dilute sulphuric acid (1 : 3) and 20 c.c. of water, 10 c.c. of nitric acid are then added, and the solution is boiled to expel nitrous fumes. After the addition of 25 grams of ammonium phosphate and 250 c.c. of water, the solution is boiled, treated with a slight excess of permanganate, boiled for a further fifteen minutes, and poured into 120 c.c. of 20% sodium hydroxide solution boiled previously with the addition of a slight excess of permanganate and then treated with 10 c.c. of 5% manganese sulphate solution; if the resulting mixture is not alkaline, more sodium hydroxide is added. After cooling, the mixture is acidified with acetic acid, diluted to 500 c.c., and filtered. If cobalt and nickel are absent, the chromium is estimated colorimetrically by comparison with potassium bichromate solution. When cobalt and nickel are present, 100 c.c. of the filtrate are boiled, sodium hydroxide is added until a precipitate forms, the solution is then cooled, filtered, the filtrate acidified with sulphuric acid, and the chromium estimated colorimetrically. W. P. S.

Qualitative Separation and Detection of Uranium, Vanadium, and Chromium when Present Together. Philip E. Browning (*J. Amer. Chem. Soc.*, 1921, **43**, 114—115).—The solution containing chromic and vanadic acids together with a uranium salt is made faintly alkaline with ammonia and then faintly acid with acetic acid and treated with ammonium phosphate. Uranium phosphate is precipitated, filtered, and washed. The uranium is confirmed by the addition to the precipitate of a drop of potassium ferrocyanide, when a reddish-brown stain is the result. The filtrate is treated with sulphur dioxide in excess to reduce the vanadic and chromic acids; the excess of sulphur dioxide is removed by boiling. Bromine is added in excess and the excess removed by boiling, this oxidises the vanadium to vanadic acid but does not affect the chromium. Ammonia is added and the chromium thrown out as a green precipitate of phosphate and hydroxide. After the removal of the chromium, the filtrate is made alkaline with ammonia and saturated with hydrogen sulphide, which gives the pink or violet oxysulphide of vanadium. J. F. S.

Tervalent Titanium. I. Volumetric Estimation of Iron by Titanous Salts. William M. Thornton, jun., and James E. Chapman (*J. Amer. Chem. Soc.*, 1921, **43**, 91—102).—The method of estimating ferric iron by titration with a solution of titanous chloride, using ammonium thiocyanate as indicator (Knecht and Hibbert, A., 1903, ii, 509), has been investigated and the definite conditions specified for the accurate performance of the operation.

It is shown that either titanous chloride or titanous sulphate in slightly acid solution (to prevent hydrolysis) may be employed. The titanous solution must be kept in contact with hydrogen both in the storage bottle and in the burette, and the titration must be carried out in an atmosphere of carbon dioxide. The titanous solution is standardised by means of ferrous ammonium sulphate, which is oxidised exactly to the ferric condition by potassium permanganate. The titrations should be carried out at temperatures below 30°, and the volume of the solution titrated should in no circumstances exceed 500 c.c. For a satisfactory end point the quantity of indicator used should be, unless there is any special reason to the contrary, 10 c.c. of 10% ammonium thiocyanate, and in no case should less than 2·5 c.c. be used. The presence of hydrochloric acid has no effect on the reaction, but if hydrofluoric acid is present the thiocyanate produces only a yellow coloration instead of a red one. This difficulty is surmounted by the addition of a quantity of boric acid sufficient to restore the red colour. When ferrous iron has to be estimated this should be oxidised to the ferric condition and then reduced with the titanous solution. Solutions of titanous sulphate when preserved in hydrogen maintain their titre unchanged indefinitely.

J. F. S.

Method of Estimating and Verifying the Purity of Organic Compounds by Oxidation with Chromic Acid. H. CORDEBARD (*Ann. Chim. anal.*, 1921, [ii], **3**, 49—53).—The substance is heated with sulphuric acid and a definite excess of potassium dichromate solution, and the excess of dichromate is then titrated with ammonium ferrous sulphate solution. The purity of the substance is deduced from the amount of dichromate which it reduces.

W. P. S.

Critical Temperature of Solution of Hydrocarbons in Aniline and its Application to the Analysis of Light Petroleums. N. CHERCHEFFSKY (*Ann. Chim. anal.*, 1921, [ii], **3**, 53—55).—Priority is claimed (compare A., 1910, ii, 660) as regards the method described by Chavanne and Simon (A., 1919, ii, 432, 433).

W. P. S.

Estimation of Aromatic Hydrocarbons in Mixtures of Hydrocarbons. H. T. TIZARD and A. G. MARSHALL (*J. Soc. Chem. Ind.*, 1921, **40**, 20—25T).—The method proposed depends on the determination of the "aniline point" of the mixture before and after treatment with 98% sulphuric acid; the "aniline point" is the temperature at which a mixture of equal volumes of the hydrocarbon and aniline separates into two layers when cooled down from a temperature at which it is homogeneous. The sample is shaken for thirty minutes with three times its volume of 98% sulphuric acid, the residual hydrocarbon then separated, washed, dried over calcium chloride, and its "aniline point" determined. The difference between this value and that found for the sample before

sulphonation gives directly the percentage of aromatic hydrocarbons in the mixture, that is, lowering of the "aniline point" in degrees Centigrade corresponds with the percentage of aromatic hydrocarbons present. The nature of the non-aromatic hydrocarbon is without effect on the results obtained, but unsaturated hydrocarbons must not be present. W. P. S.

Detection of Methyl Alcohol in Spirits. F. HAHN (*Pharm. Zeit.*, 1921, **66**, 134—135).—The fact that the presence of hydrochloric acid interferes with the sensitiveness of the morphine–sulphuric acid reagent used for the detection of formaldehyde resulting from the oxidation of methyl alcohol, as mentioned by Rabe (this vol., ii, 220), has been known for some time; morphine sulphate, and not the hydrochloride, should be used in preparing the reagent. W. P. S.

Detection of Methyl Alcohol in Spirits. F. RABE (*Pharm. Zeit.*, 1921, **66**, 135).—A reply to Maue (this vol., ii, 220); the author is quite aware that the resorcinol–sulphuric acid test is not new, but he recommended it as a useful confirmatory test for formaldehyde. W. P. S.

Detection of Methyl Alcohol. G. MAUE (*Pharm. Zeit.*, 1921, **66**, 169).—A reply to Rabe (this vol., ii, 220; preceding abstract). Under definite conditions and in the presence of excess of hydrochloric acid, the magenta–sulphurous acid reaction is characteristic of formaldehyde. W. P. S.

Analysis of Liquid and Gaseous Mixtures of Ether, Alcohol, and Water. IRVINE MASSON and T. LAWSON MCEWAN (*J. Soc. Chem. Ind.*, 1921, **40**, 29—32T).—Fleischer and Frank (A., 1907, ii, 655) have given an approximate method for the analysis of a mixture of water, ethyl alcohol, and ethyl ether, the sample being shaken with water and paraffin ("benzin"), and the increase in volume of the oil being taken as the volume of ether present. This method involves the two assumptions, that all the ether is extracted by the oil, and that no change in volume takes place when ether is mixed with aqueous alcohol. The authors find that neither of these assumptions is correct, the results actually obtained being inaccurate by about 10% for the ether and by considerably more than this for the alcohol.

If, however, the extraction is effected by means of paraffin and water, and due allowance is made for the partition of ether and alcohol between the two layers, the ether content of a sample may be found accurately to within 1%. Further, if this result and the density of the sample are compared with actual experimental data for the densities of synthetic tertiary mixtures, the alcohol content may be estimated to within 1%.

With vaporous mixtures, similar principles apply to the estimation of the ether, the vapours being first absorbed in concentrated sulphuric acid; the alcohol + water are given by difference from

the increase in weight of the acid. The water vapour may be estimated separately, if required, by absorbing it in ignited alumina.

T. H. P.

Characteristic Reaction of Phenol. GEORGES RODILLON (*J. Pharm. Chim.*, 1921, [vii], **23**, 136—137).—If 10 c.c. of a solution containing phenol are treated with a drop of 10% sodium nitrite solution and then poured on the surface of concentrated sulphuric acid, a coloured zone (red above, green below) appears at the junction of the two liquids.

W. P. S.

Miscibility of Phenol and some Mineral Solutions. Analytical Applications. RENÉ DUBRISAY (*Bull. Soc. chim.*, 1921, [iv], **29**, 78—88).—A more detailed account of work already published (A., 1919, i, 73; ii, 78; 1920, ii, 508, 756).

W. G.

ββ′-Di-iododiethyl Sulphide and its Application to the Detection and Estimation of Yperite. V. GRIGNARD, G. RIVAT, and G. SCATCHARD (*Ann. Chim.*, 1921 [ix], **15**, 5—18).—ββ′-Dichlorodiethyl sulphide in acetic acid solution readily reacts with hydriodic acid to give *ββ′-di-iododiethyl sulphide*, $S(C_2H_4I)_2$, m. p. 62°. The ready formation of this compound may be made use of for the estimation of ββ′-dihydroxydiethyl sulphide or of yperite.

In the estimation of ββ′-dihydroxydiethyl sulphide 0·7—0·8 gram of this substance is weighed out into a 50 c.c. conical flask, 5 c.c. of 54—55% hydriodic acid are added, and the mixture is heated at 70—75° for fifteen to twenty minutes. The mixture is cooled, filtered through glass wool, the precipitate being washed with water. In the filtrate the free iodine is estimated by titration with $N/10$-thiosulphate and then the acidity with N-sodium hydroxide, using phenolphthalein as an indicator. If these two titrations give B c.c. and A c.c. respectively, and a blank estimation without any hydroxyethyl sulphide gives B_0 c.c. and A_0 c.c., then the weight of dihydroxydiethyl sulphide in the sample weighed out is $61[A_0 - A - (B - B_0)/20]$ mg.

In the estimation of yperite 5 c.c. of 54% hydriodic acid and 15 c.c. of acetic acid are heated at 70° for fifteen minutes under an air condenser, and the mixture is then cooled and made up to 500 c.c. In 50 c.c. of this solution the iodine is liberated by the addition of 10 c.c. of a 10% solution of sodium nitrite. The iodine is extracted with carbon tetrachloride, the extract is washed with water, and the free iodine in it titrated with $N/10$-thiosulphate, A_0 c.c. being required.

A second operation is carried out, 1 gram of yperite being heated, this time with the hydriodic and acetic acids, but before making the volume up to 500 c.c., 100 c.c. of carbon tetrachloride is added. The mixture is vigorously shaken, and the two layers are then allowed to separate. From the aqueous layer (400 c.c.) 50 c.c. is taken and titrated with $N/10$-thiosulphate, A_1 c.c. being required. The 100 c.c. of carbon tetrachloride is now carefully separated,

and the free iodine in it is titrated with the $N/10$-thiosulphate, A_2 c.c. being required. Then, if exactly P gram of yperite was weighed out, the sample contained $[10A_0+1\cdot5-8A_1-A_2]0\cdot82/P\ \%$ of yperite.

For the detection of yperite a solution containing 20 grams of sodium iodide, 40 drops of a 7·5% solution of copper sulphate, and 2 c.c. of a 35% solution of gum arabic in 200 c.c. is used. To 4 c.c. of the yperite solution 1 c.c. of this reagent is added, and a turbidity is produced after an interval of time varying with the temperature and the dilution of the yperite solution. In this way it is possible to detect 0·05 gram of yperite per cub. metre of air, after bubbling the air slowly through the reagent. W. G.

New Method for the Volumetric Estimation of Reducing Sugars. AL. IONESCU and V. VARGOLICI (*Bul. Soc. Chim. România*, 1920, **2**, 38—45).—The solution recommended contains 46 grams of potassium ferricyanide and 46 grams of potassium hydroxide in 1 litre. For an estimation, 10 c.c. of this solution is diluted with 20 c.c. of water and heated to boiling, and the sugar solution run in drop by drop until the colour just disappears. The end-point is made clearer if 10 drops of a 1% solution of picric acid are added. The latter reagent in alkaline solution in the presence of a reducing agent is converted into red picramic acid. In estimating sugar in urine, more accurate results are obtained if the urine is first defecated with lead acetate, the lead being subsequently precipitated with sodium carbonate. For the estimation of lactose in milk, the milk is first clarified by means of a 1% solution of picric acid in 2% acetic acid. In all these estimations the concentration of the sugar solution should not exceed 1%. The ferricyanide solution should be standardised against pure dextrose and 10 c.c. should be equal to 0·05 gram of dextrose.
W. G.

Quantitative Estimation of Blood Sugar with the Aid of Methylene-blue. W. EISENHARDT (*Münch. Med. Woch.*, 1920, **67**, 1382—1383; from *Chem. Zentr.*, 1921, ii, 343).—The process depends on the observation of Williamson (*Brit. Med. Journ.*, 1896) that decolorisation occurs within a few minutes when 40 c.c. of blood of a diabetic patient is heated with alkaline methylene-blue solution (1 : 6000) on the water-bath, whilst about three times this amount of normal blood is necessary to produce the same effect. An estimate of the amount of reducing substances can be formed if diminishing quantities of blood or serum are heated with methylene-blue in alkaline solution and the limits of the change of colour are observed. H. W.

Bang's Micromethod for the Estimation of Dextrose. SVEND AAGE HOLBØLL (*Biochem. Zeitsch.*, 1921, **113**, 200—209).—According to the author, 0·265 c.c. of 1/100 potassium iodate corresponds with 0·1 mg. of dextrose in Bang's new micromethod. It is also advisable to boil for six minutes in order to obtain the best results. S. S. Z.

Volumetric Method for the Estimation of Lactose by Alkaline Potassium Permanganate. FELIPE T. ADRIANO (*Philippine J. Sci.*, 1920, **17**, 213—220).—A mixture of 50 c.c. of $N/10$-permanganate solution, 25 c.c. of 0·848% sodium carbonate solution, 10 c.c. of lactose solution (containing about 1·5 % of the sugar) and 15 c.c. of water is heated at 95° for two minutes, 25 c.c. of 30% sulphuric acid are then added, and the mixture is titrated with $N/10$-oxalic acid solution until the liquid is clear. The excess of oxalic acid is titrated with $N/10$-permanganate solution. The quantity of permanganate used for the oxidation is a measure of the amount of lactose present; the permanganate solution must be standardised against pure lactose. A table is given showing the amounts of permanganate corresponding with quantities of lactose varying from 1 to 40 mg. The method may be applied to the estimation of lactose in milk after this has been treated with copper sulphate, nearly neutralised, and filtered; the results obtained are slightly lower than those yielded by the Soxhlet method. W. P. S.

Reagent for Wood and Vanillin. J. GRÜSS (*Ber. Deut. bot. Ges.*, 1921, **38**, 361—368).—The reagent is prepared by dissolving vanadium pentoxide in dilute phosphoric acid solution. When a wood shaving is treated with this solution, the cell walls are gradually coloured yellowish-brown. A reddish-brown precipitate is produced when vanillin is added to the reagent; if the test is made on a microscope slide, the formation of red-brown crystals may be observed. W. P. S.

The Estimation of Bile Acids in Bile. CARL L. A. SCHMIDT and A. E. DART (*J. Biol. Chem.*, 1921, **45**, 415—421).—Hydrolysis of the bile acids with sodium hydroxide yields glycine and taurine, which can be estimated together by the reaction of their amino-groups with nitrous acid. Taurine can be estimated separately by an analysis of the sulphur, and from these two determinations the amounts of glycocholic and taurocholic acids may be estimated.
J. C. D.

Detection of Acetone in Urine. H. CITRON (*Deut. med. Woch*,. 1920, **46**, 1439; from *Chem. Zentr.*, 1921, ii, 432—433).—The apparatus recommended for the distillation of acetone from the urine under investigation, consists of a glass bulb of about 250 c.c. capacity, open at the top and drawn out at the bottom to a solid rod to which a small, saucer-like cup is fixed. In use, urine (50 c.c.) is placed in a beaker immersed in water heated previously to its boiling point; the bulb is filled with cold water, and placed on the beaker, the contents of which are boiled during three minutes. The distillate collects in the little cup and is tested for acetone in the usual manner. H. W.

General and Physical Chemistry.

The Law of Moduli and the Theory of Electrolytic Dissociation. Determination of Moduli of Refraction. VICTOR J. BERNAOLA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 17—31 and 73—99).—An exposition of Valson's law of moduli applied to solutions of electrolytes is given with special reference to earlier work on indices of refraction and refractive powers. The earlier observations have been supplemented by the author, using normal and decinormal solutions at 20° and 30° respectively. Moduli of refraction have been calculated for a number of kations and anions both in normal and decinormal solutions. It is shown that the temperature effect is negligible. Whilst refractive indices of solutions calculated from the moduli obtained are in good agreement with observed values when only normal or decinormal solutions are considered, the moduli obtained from the observations on normal solutions do not give satisfactory results when used for the calculation of refractive indices of decinormal solutions and vice versa. G. W. R.

Dispersion of Hydrogen in the Ultra-violet. MAX KIRN (*Ann. Physik*, 1921, **64**, 566—576).—The refractive index of hydrogen for the green mercury line $\lambda 5462$ was determined absolutely: $(n-1).10^6 = 139{\cdot}65$. The dispersion was measured to $\lambda 1854$ and can be represented by the formula $(n-1).10^8 = 13610{\cdot}1866 + 1{\cdot}0246373 \times 10^{10}\lambda^{-2} + 990606{\cdot}9 \times 10^{10}\lambda^{-4} + 70{\cdot}512617 \times 10^{20}\lambda^{-6}$. The value of $n-1$ increases more rapidly with λ than according to Debye's formula. J. R. P.

The Spectrum of Hydrogen Positive Rays. L. VEGARD (*Phil. Mag.*, 1921, [vi], **41**, 558—566).—The differences found by Thompson (see A., 1920, ii, 521) in the spectra of hydrogen positive rays are ascribed to chance variations in pressure and the energy of the rays. Light is emitted both when the positively charged atom is neutralised and when the neutral atom collides with the molecules of the gas. J. R. P.

The Spectrum of Hydrogen Positive Rays. G. P. THOMPSON (*Phil. Mag.*, 1921, [vi], **41**, 566—567).—A reply to the criticism of Vegard (see preceding abstract). The latter does not explain the correlation shown to exist between the ratio of the intensities of the spectra and the proportion between the atoms and molecules of hydrogen in the rays as determined directly. J. R. P.

The Vacuum Arc Spectra of Sodium and Potassium. SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1921, A., **99**, 69—77).—The wave-lengths of the sharp and diffuse series of lines of sodium

and potassium were measured in a source giving well-defined lines. Channelled-space emission bands were observed in the light from a sodium vapour lamp and their heads measured approximately. The combination line $1s - 2d$ in potassium has been resolved into a pair, the wave-lengths of which were measured. The presence of potassium in the sun was established and some additional sodium lines were identified with solar lines. J. R. P.

Some Spark Spectra in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1921, **172**, 803—805).—The spark spectra are given for zinc over the range $\lambda = 1840$ to 1440, for cadmium over the range $\lambda = 1850$ to 1420, and for lead over the range $\lambda = 1822$ to 1406. W. G.

The Spark Spectra of Iron and Cobalt in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1921, **172**, 851—854).—The spark spectra of iron over the range $\lambda 1845$ to 1530 and of cobalt over the range $\lambda 1845$ to 1455 are given. The rays are generally weak; many are classed as diffuse or broad and many are probably double or multiple. W. G.

Rotation Spectra and Isotopy. ARTHUR HAAS (*Zeitsch. Physik*, 1921, **4**, 68—72).—A theoretical paper in which the rotation spectrum is discussed and it is shown that the three different forms of the rotation spectrum, the pure rotation spectrum, the vibrational rotation spectrum, and the band spectrum are to be represented by the equations (i) $\nu = \gamma/J$, (ii) $\nu - \nu_0 = \gamma/J$, and (iii) $\nu - \nu_0 = \gamma_1/J_1 - \gamma_2/J_2$ in which J_1 and J_2 are the moment of inertia before and after electron transference, ν_0 the fundamental frequency, and γ, γ_1, and γ_2 quantities dependent on the quantum number. Hence with a given quantum number and a given fundamental frequency the vibration number is a function of the molecular moment of inertia alone, from which it appears possible to obtain spectroscopic evidence of isotopy. J. F. S.

Functions of Chromophores. VII. Optical Properties of some Heavy Metal Complexes. II. I. LIFSCHITZ and ERNST ROSENBOHM (*Zeitsch. physikal. Chem.*, 1921, **97**, 1—14. Compare A., 1920, ii, 208).—The absorption spectra of a number of derivatives of cobalt, chromium, manganese, iron, osmium, platinum, rhodium, and several organic substances has been investigated. The spectra obtained from solutions exhibit similar wide, flat, and somewhat diffuse bands which are in all probability made up of a series of narrow, sharper bands. To test this point, the absorption spectra of the vapour of osmium tetroxide, the triacetylacetonates of cobalt, chromium, and iron, nickel carbonyl, quinone, and ferric chloride were examined. It is found that only in the case of osmium tetroxide and benzoquinone was the desired spectrum observed, in the former case twelve bands between $\lambda 2313{\cdot}2$ and $\lambda 3111{\cdot}9$ were observed, whilst in the latter case nine bands between $\lambda 4030$ and $\lambda 4769$ were obtained. In the case of benzoquinone the bands form a series which is represented by the formula

$\nu = 2096{\cdot}9 + 35{\cdot}4n + 1{\cdot}3m$, where n is a whole number lying between 3 and 10, and m one of the whole numbers, 0, 6, 4, 9, 11, 15, and 23. J. F. S.

Functions of Chromophores. VIII. Chromophores of Conjugated Compounds. I. LIFSCHITZ (*Zeitsch. physikal. Chem.*, 1921, **97**, 15—21. See preceding abstract).—A discussion of Ley's remarks on the constitution of conjugated salts of 1—3 diketones (A., 1920, ii, 571). J. F. S.

Absorption Spectra of Potassium Ferro- and Ferricyanides. FREDERICK H. GETMAN (*J. Physical Chem.*, 1921, **25**, 147—159).—The absorption spectra of the α- and β-ferrocyanides of potassium are identical, which is in favour of the non-isomeric character of these salts. A slight but well-defined difference between the absorption spectra of the α- and β-ferricyanides of potassium was established, confirming the isomeric character of the salts. There is a marked difference between the absorption spectra of ferrocyanides and ferricyanides of potassium. On the assumption that an absorption band indicates potential tautomerism in the molecule, a modification of the formulæ proposed by Friend (T., 1916, **109**, 718) offers a possible explanation of the presence of bands in the absorption spectra. The relative number and position of the tautomeric groups may be the cause of the marked differences between the absorption spectra of ferro- and ferri-cyanides of potassium. J. R. P.

The Absorption of Light by Reduced Hæmoglobin. PAUL HÁRI (*Biochem. Zeitsch.*, 1921, **115**, 52—62).—The absorption of light by reduced hæmoglobin has been determined along a large part of the visible spectrum. The maximum absorption occurs at $555{\cdot}3\mu\mu$. S. S. Z.

Spectrophotometry in the Visible and Ultra-violet Spectrum. T. R. MERTON (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 78—84).—The dispersing system (for example, prism) is crossed with a very coarse grating and the length of the slit reduced to a very small value. The grating is inserted between the prism and the camera lens with the rulings perpendicular to the refracting edge of the prism. A continuous spectrum then appears on the plate as a dark central strip with a succession of other strips of different intensities on each side. In the case of a discontinuous spectrum, the "lines" consist of dots of different intensities on each side of the central dot. If the last dots visible in the case of two lines are noted, previous knowledge of the relative intensities of the different orders corresponding with these dots enables the relative intensities of the lines to be determined. The gratings were constructed by ruling a smoked quartz plate and calibrated with a neutral wedge. J. R. P.

Polarisation and Intensity of the Fluorescence of Iodine Vapour and its Dependence on Temperature. PETER PRINGSHEIM (*Zeitsch. Physik*, 1921, **4**, 52—60).—The partial polarisation

of the fluorescence of iodine vapour is within the temperature range 20—350° independent of the temperature; this fact, despite the increase in the velocity of rotation of the molecule, is to be expected on theoretical grounds. The intensity of the fluorescence on warming over the temperature range 20—350° decreases only slightly, the relative values being 20°, 100; 100°, 99; 200°, 97·5; 300°, 94·5; and 350°, 92·4. Thus the weakening of the fluorescence by increasing the vapour density is not to be explained by the shortening of the mean impact time alone. J. F. S.

The Influence of Light on the Conductivity of Fluorescent Liquids. H. SOULAN (*Compt. rend.*, 1921, **172**, 581—582).—The prolonged illumination of a fluorescent liquid results in a progressive variation of the electrical conductivity, ending in the establishing of a limit value, which should remain after return to darkness. The results with a number of fluorescent substances in very dilute solutions give the equation $\log (C_\infty - C_t) = b - at$, C_t being the conductivity at a time t, C_∞ the limit value, and a and b two constants characteristic of the fluorogen. W. G.

Colour and Optical Activity in Organic Compounds. ERNESTO LONGOBARDI (*Anal. Soc. Quím. Argentina*, 1920, **8**, 153—161).—The possibility of an antagonism between optical activity and colour in organic compounds was suggested in an earlier paper by the author (A., 1913, ii, 368). This question is discussed further in the present paper. Coloured compounds exist which, from their structure, should exhibit optical activity. Where optical activity has been verified, certain anomalies occur and, further, the materials used have been of doubtful purity. Unsuccessful attempts were made by the author to resolve alkali-blue and nitrotyrosine, obtained from *l*-tyrosine. G. W. R.

Photolysis of Water. EMIL BAUR and A. REBMANN (*Helv. Chim. Acta*, 1921, **4**, 256—262).—The fact that, when two unattackable electrodes are polarised in the solutions of certain colouring matters sensitive to light and then illuminated, alterations of potential occur at the electrodes and consequently depolarisation currents are originated, is best explained on the assumption that the colouring matter produces a photochemical decomposition of the water, but to such a slight extent that no visible evolution of detonating gas takes place (compare Staehelin, A., 1920, ii, 580). The authors experimented with solutions of uranyl salts, eosin, rhodamine, quinine, etc., in an exhausted vessel with the help of the differential tensimeter, but no sign of the evolution of oxygen or hydrogen was observed. The use of depolarisers also led to no definite result. The apparent rarity of chemical light actions is conditioned by the fact that the primary products of photolysis are usually capable, either by a reaction in the dark or by a second photolytic process opposed to the first, of re-forming the original compounds; the total chemical effect of the light is thus nil. The results obtained show that it is difficult to break into such a reaction cycle by addition of depolarising agents. T. H. P.

Primary Effect of Light and Photochemical Valency. P. R. KÖGEL (*Photogr. Korr.*, 1920, **57**, 308—310; from *Chem. Zentr.*, 1921, i, 553).—The primary photochemical effect consists in the activation of additional valency, which is only possible when energy is supplied, and leads first of all chemically to the formation of additive compounds. The effect of a photochemical catalyst is similar, and can hence lead to the formation of an endo-energetic product, the catalyst reverting to its original state of energy. Such an action can be attributed to chlorophyll. Other photochemical reactions can be attributed to the formation or breaking up of polymerides. Photostereochemical grouping is also closely related. The activation of silver bromide by dyes can be explained as follows. The light raises the valency of single atoms in the dye molecule; the bromine will not be set free from the silver by the partly actinic rays, for example, yellow, but its union will be loosened; the bromine will then tend to react with the additional valency of the dye, without, however, a compound necessarily being formed. The dye, as is already believed, only acts catalytically. G. W. R.

Optical Properties of Disperse Systems. I. Colour Changes through Illumination. FRITZ WEIGERT (*Kolloid Zeitsch.*, 1921, **28**, 115—124).—When silver chloride gelatin emulsion, which has been exposed to light until a bluish-red colour is produced and then washed to remove excess of silver nitrate, is exposed to light of various colours, the emulsion assumes approximately the colour of the exciting light. In all cases the extinction in the existing colour is decreased by the treatment, but in all other colours it is increased. The change is shown to be entirely physical, due to a change in the silver chloride–silver system. When the exciting light is linearly polarised, the isotropic layer assumes the properties of double refracting crystals, the extinction direction of which lies in the intersecting line of the vibration plane of the electrical and magnetic vector of the exciting radiation with the layer. When the exciting light is first applied the layer is positively dichroic in all colours other than the exciting colour; when the treatment is long the dichroism changes its sign. The effect of light weakens with decreasing wave-length, particularly in the case of the double refraction and the dichroism. The extinction is equally strong in the green and blue and decreases from yellow to the red, so that the colour of the layers is always red. The sensitiveness does not run parallel with the extinction; the maximum in this case lies in the red. It is shown that the above phenomena occur also in other cases. Collodion layers of the cyanine dyes are the most sensitive, but collodion layers of most sensitising dyes, such as pinachrome, pinacyanol, pinaverdol, orthochrome, homocoll, and ethyl-red also exhibit the same phenomena.
J. F. S.

Action of Light on Silver Bromide. I. WALTHER EHLERS and PETER PAUL KOCH (*Zeitsch. Physik*, 1920, **3**, 169—174).—With the object of ascertaining the course of the action of light on

silver bromide, the authors have determined the change in weight which occurs when particles of silver bromide of an average diameter $0{\cdot}4\mu$ are illuminated. The method consisted in placing particles of silver bromide in a condenser and determining the potential which must be applied to keep the particle suspended. A beam of light is then allowed to fall on the bromide and the change in the potential ascertained at intervals of time. It is found that when the condenser is filled with air the mass of the particles increases slightly by an amount corresponding with an increase in potential of 1·5 volts; on the other hand, if the condenser is filled with nitrogen, it is found that with larger particles the weight decreases 1·5—5·0%, whilst with the smallest particles the decrease is 10%. From these data it becomes possible to calculate the mass of the latent image, and the amount of bromine given up by the particles on illumination. Calculations show that a particle of silver bromide of weight 3×10^{-12} gram loses, on illumination for twenty minutes by an arc lamp, 6% of its weight of bromine. Comparative experiments with a specially rapid silver bromide gelatin plate show that the bromide particle, when illuminated for 1/100 sec. by a light intensity 1/10000 of that used in the above experiments, loses $1{\cdot}5 \times 10^{-22}$ gram of bromine, that is, approximately one atom per particle. J. F. S.

Optical Properties of Disperse Systems. II. Significance of the Amicroscopic Phase. FRITZ WEIGERT and HANS POHLE (*Kolloid Zeitsch.*, 1921, **28**, 153—161. Compare this vol., ii, 289).—A continuation of work previously published (*loc. cit.*) undertaken with the object of ascertaining whether the ultramicroscopic examination of changes which occur when photo-sensitive chlorides are exposed to light is capable of furnishing knowledge of the changes occurring in the individual particles of a colloidal system. The results, as far as the main object of the work is concerned, are negative, since it is shown that the secondary particles, which alone are responsible for the change, are not resolvable ultramicroscopically. The absorption displacement and the dichroic effect brought about by light is due to the action on the amicrons of the light-sensitive chlorides which are closer together than the wave-length of the exciting light. It is calculated that the portion of the photo-chloride which is affected by these optical amicrons amounts to at least 36%. It is shown that the optical properties of the system are due to amicroscopic micellæ which are nearer together than the wave-length of the light used.
J. F. S.

The Influence of Light Energy on the so-called Exchange or Displacement Reactions. Reduction of Alkali Nitrite. OSKAR BAUDISCH (*Ber.*, 1921, **54**, [*B*], 413—417).—Reactions of the type of the reduction of nitrite by potassium ferrocyanide and oxygen (A., 1917, i, 434) are found to be very susceptible to the influence of light. Thus, a freshly-prepared-solution of potassium ferrocyanide is unchanged by a solution of nitrosobenzene or *p*-nitrosodimethylaniline in the dark, but rapidly darkens in colour

on exposure to light owing to the formation of the compounds $\left[Fe^{Ph\cdot NO}_{(CN)_5}\right]Na_3$ and $\left[Fe^{NMe_2\cdot C_6H_4\cdot NO}_{(CN)_5}\right]Na_3$. The newly-introduced group can be again displaced if an excess of sodium cyanide or sodium nitrite is added to the solutions which are kept exposed to light. Similarly, one cyano-group of potassium ferrocyanide is readily displaced by oxygen, with the formation of an intensely yellow peroxide, $\left[Fe^{O_2}_{(CN)_5}\right]K_3$, when aqueous solutions are exposed to light and air, and the compounds, $\left[Fe^{NH_3}_{(CN)_5}\right]Na_3$ and $\left[Fe^{OH_2}_{(CN)_5}\right]Na_3$, are autoxidisable with still greater ease.

The following experiments are designed to show that subsidiary valencies are operative in these exchange reactions. Among organic compounds, pyridine has the greatest affinity for iron, union occurring with the iron atom by means of the subsidiary valency of the tervalent nitrogen atom. If this is actually the case, 2-methylpyridine must be considerably less active, since its subsidiary nitrogen valency is partly diverted by the neighbouring methyl group. This is shown to be the case by mixing solutions of $\left[Fe^{NH_3}_{(CN)_5}\right]Na_3$ with pyridine and α-picoline and adding aqueous alcoholic solutions of nitrosobenzene. In the absence of base, an intense violet colour is immediately developed; with pyridine, the nearly colourless solution gradually becomes pink, whilst with α-picoline an intense wine-red colour is produced which becomes as dark violet as the control solution. The percentage of pyridine in technical α-picoline can be estimated approximately in this manner. H. W.

Photo-bromination of Toluene and Xylene. TORSTEN SWENSSON (*Zeitsch. wiss. Photochem.*, 1921, **20**, 206—218).—The rate of absorption of bromine by toluene and xylene in the presence of benzene, alcohol, carbon tetrachloride, or hydrogen bromide, when exposed to light from a quartz mercury lamp at 20°, has been investigated. The results show that alcohol has a negative catalytic action on the process owing to its removal of the hydrogen bromide from the sphere of action. Hydrogen bromide catalyses the reaction very strongly in the positive sense, and at the same time it is decomposed. J. F. S.

Collisions between Atoms and Free Electrons. O. KLEIN and S. ROSSELAND (*Zeitsch. Physik*, 1921, **4**, 46—51).—A theoretical paper in which the effects of collisions between atoms and free electrons are considered. The authors regard such collisions as of two kinds, (1) collisions of the first kind studied by Franck and Hertz (A., 1919, ii, 206) in which a change of the atomic system, without the emission of rays, from the normal condition to a stationary condition with greater energy is brought about whilst the electron loses a definite amount of energy in keeping with the energy principle and (2) collisions of the second kind, in which

the atom, without emission of radiation, passes from a stationary condition of greater energy content to a stationary condition of smaller energy content, whilst the electron after the completion of the collision possesses a greater kinetic energy, the amount of the increase being equal to the energy lost by the atom.
J. F. S.

Precision Measurements in the X-Rays Spectra. IV. K. Series, the Elements Copper to Sodium. ELIS HJALMAR (*Phil. Mag.*, 1921, [vi], **41**, 675—681).—See A., 1920, ii, 655.

Fine Structure of the Röntgen Spectra. ADOLF SMEKAL (*Zeitsch. Physik*, 1921, **4**, 26—45).—A theoretical paper in which an attempt is made to extend in two directions the position reached by the Kossel-Sommerfeld considerations of the fine structure of the Röntgen spectra. Kossel and Sommerfeld make use of hydrogen-like energy levels for the individual electron sheaths. The present work subdivides the sheath as a whole into three quantum numbers, and postulates sheath conditions, in which all the electrons do not behave similarly. The first assumption explains satisfactorily all the sheath conditions, including those which are unlike hydrogen, corresponding with the absorption edges of the individual Röntgen series, if none of the quantum numbers can become zero. The second assumption appears to be of importance for the K sheath, and on this basis an explanation of the fine structure of K_{α} is attempted. It is also shown that the L series contains only three absorption edges, the Λ doublet of the L series is not real, the K_{α_3} and K_{α_4} lines of Siegbahn as well as the K_{α_5} and K_{α_6} lines of Hjalmar have, as has K_{α}, two quantum levels.
J. F. S.

Interpolation Table for the Calculation of Spectral Series. ANGEL DEL CAMPO and MIGUEL CATALÁN (*Anal. Fís. Quím.*, 1920, **18**, 118—128).—Rydberg's tables for the calculation of spectral series are recalculated, using the more recent value for the constant N, found by Curtis (A., 1914, ii, 761).
G. W. R.

The Corpuscular Spectra. Laws of the Photo-electric Emission for High Frequencies. MAURICE DE BROGLIE (*Compt. rend.*, 1921, **172**, 806—807. Compare this vol., ii, 232, 323).—In illuminating a certain radiator, A, with a ray of light, X, of frequency ν, the Bohr's rings of the radiator corresponding with the work of extraction W_K, W_L, W_M, etc., for the emission of electrons, a series of corpuscular rays may be observed having for quanta $h\nu - W_K$, $h\nu - W_L$, $h\nu - W_M$, ..., if the frequency ν is superior to the frequency K. The radiator A also gives fluorescent rays which furnish corpuscular rays.
W. G.

Relative Ionisation of Different Gases by α-Rays. VIKTOR F. HESS and MARIA HORNYAK (*Wien. Anzeiger*, 1920, 219; from *Chem. Zentr.*, 1921, i, 552—553).—Measurements were made of the total ionisation by α-rays from polonium of carbon dioxide, nitrogen,

oxygen, hydrogen, and coal gas compared with that of air. For carbon dioxide, using the full range of the radiation, it was about 23% greater and for coal gas about 12% less than for air. By restricting the range of the radiation used, that is by using α-rays of smaller velocity, quite different relative values were obtained, from which it is concluded that the form of the Bragg curve is notably different for the different gases, particularly in the terminal portion of the range. For example, using the last three millimetres of the range, the ionisation for carbon dioxide was 8% smaller, for coal gas 22% smaller, but for hydrogen 25% greater than for air. G. W. R.

Disintegration of Atoms by α-Particles. (SIR) E. RUTHERFORD and J. CHADWICK (*Nature*, 1921, **107**, 41).—The hydrogen atoms expelled from a hydrogen compound on bombardment with α-particles have a range of 29 cm. in air; those from nitrogen 40 cm. Long-range hydrogen atoms were similarly liberated from boron, sodium, fluorine, aluminium, and phosphorus. They are not liberated from oxygen, sulphur dioxide, or carbon dioxide molecules. The following elements showed little if any effect with an absorption corresponding with 32 cm. of air: lithium, glucinum, carbon, oxygen, magnesium, silicon, sulphur, chlorine, potassium, calcium, titanium, manganese, iron, copper, tin, and gold. The particles appear to consist of hydrogen liberated at different speeds. Assuming the law connecting range and velocity to be the same as for α-particles, it would appear that the energy of the H-particle from aluminium is about 25% greater than the energy of the incident α-particle. The conclusion is drawn that elements with atomic mass $4n$, where n is a whole number, give no particles, whilst elements with atomic masses $4n + 2$ or $4n + 3$ give the particles. Atoms of type $4n$ are supposed to be built up of stable helium nuclei; those of masses $4n + 2$ or $4n + 3$ of helium and hydrogen nuclei. J. R. P.

Different Modes of Radioactive Disintegration and the Possibility of [Indicating] their Significance from the Nuclear Structure. LISE MEITNER (*Zeitsch. Physik*, 1921, **4**, 146—156).—On the basis of the generally accepted helium hydrogen nuclear structure of the atomic nucleus, the author has deduced theoretically four different methods by which radioactive disintegration may proceed. These are (i) a series of successive α-changes, $-\alpha-\alpha-\alpha-$, (ii) an α′-change followed by two β-changes, $-\alpha'-\beta-\beta-$, (iii) a β-change which leads to branch changes leading eventually to the same product, $\beta\text{-}\overset{\beta\ \ \alpha'}{\underset{\alpha'\ \ \beta}{<>}}$, and (iv) a branching change of the form $\overset{\alpha}{\underset{\alpha'}{<}}$ or $\overset{\alpha}{\underset{\beta}{<}}$. These four modes of disintegration are considered in connexion with the known radioactive changes. J. F. S.

Mass of the Long-range Particles from Thorium-*C*. (SIR) E. RUTHERFORD (*Phil. Mag.*, 1921, [vi], **41**, 570—574).—In the disintegration of thorium-*C* a small number of particles with the

long range of 11·3 cm. are expelled, which were supposed to be atoms of helium. On account of the possibility that these may have originated by collision of the α-particles with the oxygen of the mica, the experiments were repeated with aluminium as the absorbing screen. The same results were found (see following abstract), the number of particles being 1/10,000 of the total number of α-particles from the thorium-*C*. Examination of the deflection of the particles in a magnetic field showed that they were ordinary α-particles of mass 4. There is no information as to the source of the long-range α-particles. It may be that thorium-*C* may break up in two ways with emission of rays of ranges 8·6 and 11·3 cm., or that 1/10,000 of the atoms of thorium-*C* break up directly with emission of these very swift α-particles. The resulting product would have the atomic number 81, which is that of an isotope of thallium of atomic weight 208. The amount of thallium found in thorium minerals should be about 0·00004%. J. R. P.

Long-range Particles from Thorium Active Deposit. A. B. Wood (*Phil. Mag.*, 1921, [vi], **41**, 575—584; see also preceding abstract).—The emission of long-range particles from thorium active deposit was re-examined. The ratio of the total number of particles with ranges exceeding 8·6 cm. to the total number of ordinary α-particles (ranges 5·0 and 8·6 cm.) is 1 to 11,000. At least 90% of the long-range particles originate in the active deposit, whilst the remainder are probably produced by collision of α-particles with oxygen atoms in the mica screen employed to stop the short-range particles. Slight evidence was obtained of the existence of high-velocity particles, probably hydrogen atoms, of ranges exceeding 11·3 cm. The proportion of these to the total number of long-range particles is probably not more than 1 in 100. J. R. P.

Volatilisation of Thorium-*B* and Thorium-*C* deposited on Gold. Stanislaw Loria (*Krakauer Anzeiger*, 1917, 260—264; from *Chem. Zentr.*, 1921, i, 608).—The volatilisation of a radioactive product deposited on metal was examined in the case of thorium-*B* + thorium-*C* deposited on gold. The volatilisation of thorium-*B* from gold begins sooner than from platinum and palladium and throughout the temperature interval 300—1000° is greater from gold than from the other two metals. The volatilisation of thorium-*C* from gold is very similar to that from platinum. In both cases there occurs a discontinuity on the volatilisation curve at about 760°, which may be referred to the occurrence of thorium-*C* oxide, stable in this region of temperature. This discontinuity is not shown for thorium-*C* on palladium. G. W. R.

The Isotopism of Mesothorium and Radium and the Separation of these Elements from Barium. Ralph K. Strong (*J. Amer. Chem. Soc.*, 1921, **43**, 440—452).—To ascertain whether mesothorium and barium are truly isotopic, experiments were made in which barium compounds from monazite residues, containing mesothorium and radium, were subjected to fractiona-

tion, the ratio of mesothorium to radium being determined both before and after the concentration of the radioactive elements. By fractional crystallisation of the hydroxide, starting with 1,100 grams of barium chloride containing 11 mg. of mesothorium and 3 mg. of radium, there were obtained a rich fraction of 17 grams of barium chloride containing 8·4 mg. of mesothorium, and a poor fraction containing 0·22 mg. in 746 grams. The rich fraction was converted into bromide and by fractional crystallisation, 0·55 gram of crystallised barium bromide was obtained containing 6·4 mg. of mesothorium. The bromide process is much more efficient than the hydroxide process for concentrating the radioactive elements. The ratios of mesothorium to radium in the rich and poor fractions from the hydroxide fractionation and in the rich bromide fraction were found to be identical with the ratio in the original material. Radium and mesothorium are therefore true isotopes. E. H. R.

General System of the Isotopes. A. VAN DEN BROEK (*Physikal. Zeitsch.*, 1921, **22**, 164—170).—A theoretical paper in which the conditions of a schematic representation of the isotopes are discussed. J. F. S.

Absorption of Gases in the Electric Discharge Tube. F. H. NEWMAN (*Proc. Physical Soc.*, 1921, **33**, 73—82).—Various elements were deposited in a pure condition on the cathode in an electric discharge tube. To obtain a clean surface of the element the latter was distilled in a vacuum. An electric discharge was passed through nitrogen contained in the tube. Measurements were made to compare the amount of gas absorbed by the element with the quantity of electricity passing. Potassium, sodium, mercury, cadmium, antimony, magnesium, calcium, zinc, tin, phosphorus, sulphur, and iodine were used. The rates of absorption were very great with the last three elements. Hydrogen was also used in the tube and absorption occurred with phosphorus, sulphur, and iodine. The absorption is attributed principally to chemical action. Nitrogen and hydrogen assume active modifications when exposed to an electrical discharge at low pressure. J. R. P.

Mobility of Ions which are Common with those of the Solvent. G. VON HEVESY (*Zeitsch. Elektrochem.*, 1921, **27**, 21—24).—A theoretical paper in which the abnormally large mobilities of the hydrogen and hydroxyl ions are discussed. It is shown on the basis of Noyes's electrical conductivity measurements that the abnormally high mobilities of the hydrogen- and hydroxyl-ions vanish at high temperatures, and therefrom it follows that the ions of water migrate according to the same laws as other ions. A comparison of the mobility of the hydrogen ion and the hydrogen molecule shows that the latter migrates very rapidly in comparison with the "normal" ions and is only one and a half times slower than the hydrogen ion. This fact is opposed to the hypothesis that the hydrogen- and hydroxyl-ions migrate in a manner different from that of the other ions. The viscosity of water is calculated to 0·001205 at 218° and 0·000927 cg. at 306°. J. F. S.

Chlorine Overvoltages. EDGAR NEWBERY (T., 1921, **119**, 477—486).

Explanation of the Electrical Phenomena during the Decomposition of Ammonium Amalgam. GERTRUD ARONHEIM (*Zeitsch. physikal. Chem.*, 1921, **97**, 95—133).—The expulsion of positive carriers of electricity from the surface of decomposing ammonium amalgam has been examined quantitatively and the process compared with the expulsion of carriers of electricity from the surface of pure mercury when gases are bubbled through it. It is shown that both processes exhibit exactly the same regularities. They give rise to carriers charged in the same sense and have similar pressure and temperature curves. Thus the production of carriers is to be attributed to the same cause in both cases, namely, to the bubbling of gas through an electric double layer (Lenard, A., 1915, ii, 507). It is shown that bubbling ammonia through mercury does not give rise to the charged particles, whilst hydrogen and carbon dioxide produce about the same effect. It is noted that the expulsion of gas from the surface of a liquid ammonium amalgam is not visible even microscopically; this indicates an extremely fine state of subdivision of the gases. See also de Broglie (A., 1907, ii, 664), Coehn (A., 1901, ii, 155), McCoy (A., 1912, i, 539) and Becker (*Ann. Physik*, 1909, **29**, 909).

J. F. S.

Thermo-elements. I. Thermal and Electrical Conductivities of Copper-Phosphorus Alloys. GEORG PFLEIDERER (*Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 409—426; from *Chem. Zentr.*, 1921, i, 348).—The efficiency of the transformation of thermal into electrical energy by means of a thermo-element depends, not only on thermo-electrical power, but also on the ratio of thermal to electrical conductivity: the efficiency of the transformation will be less with increase of this ratio, which, according to the Wiedemann-Franz law, should remain constant.

Experiments on copper–phosphorus alloys containing 1·98 and 0·63% of phosphorus respectively failed to confirm previous observations of favourable variations in the ratio of thermal to electrical conductivity. It is concluded that there is no prospect of obtaining any increase in efficiency of thermo-elements by modification of this ratio.

G. W. R.

Thermo-elements. II. The Thermo-electric Power of Antimony–Cadmium Alloys of about 50 Atomic per Cent. FRANZ FISCHER and GEORG PFLEIDERER (*Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 440—447; from *Chem. Zentr.*, 1921, i, 349).—Antimony–cadmium alloys of approximately atomic composition show probably the highest thermo-electric power of all metals and alloys hitherto investigated. In one and the same fragment and in different fragments of the same alloy remarkably variable values for thermo-electric power were obtained, including some higher than any hitherto observed.

Such variations suggest that the thermo-electrical properties of

this alloy are much influenced by inhomogeneity. The thermal treatment is also of importance in this connexion. Thermo-electric power is altered at higher temperatures, not only by a reversible temperature effect, but also by an irreversible alteration of the material. Amalgamation depresses thermo-electric power. Alloys prepared by fusion under a mixture of lithium and sodium chlorides showed particularly low values, which, however, were increased by subsequent heating without the covering of fused salts. G. W. R.

The Behaviour of an Unattackable Electrode in the Reaction $3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$ at Equilibrium. ALFONS KLEMENC (*Zeitsch. Elektrochem.*, 1921, **27**, 110—112).—The normal potential of the reaction $2NO_2' \longrightarrow NO + NO_3'$ at 25° was calculated by Pick (A., 1920, ii, 409) on the assumption that this reaction takes place at an unattackable electrode. The author now shows, by comparing the measured potential when a platinum electrode is in equilibrium with the system, nitric acid–nitrous acid–nitric oxide, with the calculated potentials for the three reactions: (1) $NO + 2H_2O \longrightarrow 4H + NO_3'$; (2) $NO + H_2O \longrightarrow 2H^{\cdot} + NO_2'$; (3) $NO_2' + H_2O \longrightarrow 2H^{\cdot} + NO_3'$, that the observed value agrees with that calculated for the first of these reactions, which must therefore be regarded as the electrode reaction in solutions up to 3*N*. In fairly dilute solutions (about 0·3*N*), the second reaction is superimposed on the first. The correspondence of Moore's measurements (A., 1913, ii, 467) with the thermodynamic calculations based on the assumption of $2NO_2' \longrightarrow NO + NO_3'$, was probably accidental and due to the uncertainty of the equilibrium measurements of Lewis and Edgar for the reaction $3HNO_3 \rightleftharpoons 2NO + HNO_3 + H_2O$, on which the calculation depended. E. H. R.

The Mechanism of the Exchange of Energy in the Electro-chemical Passage of an Atom to the Ionic State. RENÉ AUDUBERT (*Compt. rend.*, 1921, **172**, 753—755).—The work necessary for the solution of an electrode in a solution of one of its salts may be considered as composed of two terms; a term *w* relative to the work necessary to draw an atom from the surface of the electrode, and a term *w'* relative to the work put into play in the passage of this atom to the ionic state. Considering the transformation of a gram-atom of the electrode we have $\epsilon Qn = Nw + Nw'$, where ϵ is the tension of solution of the electrode, *n* the valency of the ion, and *N* Avogadro's constant. *Nw'* may be expressed by *Jq*, where *q* is the heat of ionisation of a gram-atom of the element considered. The value of *Nw* can be calculated from the heat of vaporisation by the equation $JL = Nw + RT$ and thus it is possible to calculate ϵ. The calculated and observed values agree well in the cases examined except for cadmium and hydrogen. W. G.

The Electrical Phenomena Accompanying the Displacement of Metals. BARLOT (*Compt. rend.*, 1921, **172**, 857—859. Compare this vol., ii, 247).—If, under the experimental conditions previously

described (*loc. cit.*), the two fragments of zinc are connected to the two poles of an electric cell having a potential difference of one or two volts the figure formed by the lines of copper crystals radiating from the fragments obtained are disymmetrical and the neutral line takes a parabolic form. If the *E.M.F.* is sufficiently great there is no metallic deposit on the zinc connected to the negative pole. The formation of these figures is attributed to the action of the electric field produced by the more electro-negative metal. This action tends to orientate the positive ions of the electrolyte along the lines of force. At the same time these ions are subjected to the forces of crystallisation and when they pass to the metallic state the figures formed are the result of these two actions.

W. G.

Relationships at Copper Anodes in Solutions of Alkali Hydroxides. FR. JIRSA (*Zeitsch. Elektrochem.*, 1921, **27**, 30—34). —The potential of a copper anode in alkali solution has been measured. It is found that the addition of telluric acid to a copper anode in alkali does not cause a gradual depolarisation as is the case with a silver anode in similar circumstances (A., 1919, ii, 264). The potential of the electrode $Cu|Cu_2O_3||$, prepared without telluric acid, sinks rapidly to zero when the polarising current is cut off, but the same electrode, when in alkali solution containing telluric acid, has a constant potential difference. The cell $(Pt)Cu|Cu_2O_3,CuO,2K_2TeO_4 7NKOH,Cu(OH)_2||NKCl|Hg_2Cl_2|Hg$ has been measured at 18° and found to have the value + 0·22 volt. When solutions of alkali hydroxides are electrolysed between copper electrodes by an alternating current of 49 periods, the copper is oxidised, even when the possibility of atmospheric oxidation is rigorously excluded, and the copper passes into solution in the univalent condition. J. F. S.

Transport Numbers of Liquid Amalgams. FRANZ SKAUPY (*Zeitsch. Physik*, 1920, **3**, 178—181).—A theoretical paper in which the explanation offered by Lewis, Adams, and Lamann (A., 1916, ii, 76) for the accumulation of the dissolved metal at the anode during the electrolysis of sodium and potassium amalgams is discussed. The author shows that the mercury ions wandering to the cathode force the residue of the solution, which contains the alkali metal, to the anode. The transport number, n, is connected with the concentration of the amalgam, c, the electron concentration of the mercury, and the degree of hydrargyration of the mercury ion, z, by the formula $n = u/v(1 + z) . c/100$, where u and v are the migration velocities of the complex mercury ions and the electrons respectively. J. F. S.

Electro-endosmosis and Ion Adsorption. A. GYEMANT (*Kolloid Zeitsch.*, 1921, **28**, 103—114).—A method for the determination of electro-endosmosis is described which makes it possible to use any type of membrane. Making use of this new apparatus, the electro-endosmosis of a number of solutions has been investigated, using membranes of collodion, kaolin, carbon, agar, ferric

oxide, and filter paper. It is shown that the charge on which the electro-endosmosis depends can be attributed to ionic adsorption and in this connexion the nature of the adsorbent and the different adsorptions of the two ions are determinative. The adsorbent has the character of an acid, a base, or an ampholyte. The acid and basic membranes can be charged to the highest extent by hydrogen- or hydroxyl-ions respectively, but not discharged by these ions. In certain cases, it is possible to discharge these by tervalent ions. Ampholytes may be discharged by finite concentrations of hydrogen- and hydroxyl-ions. The so-called indifferent diaphragms behave either as acid or as ampholytic diaphragms, and correspondingly are only chargeable or dischargeable. Non-dischargeable but always negatively charged diaphragms are represented by collodion and agar, whilst the only known representative of a dischargeable membrane is charcoal. The analytically determined adsorption of an electrolyte furnishes no direct evidence on the charging produced by the electrolyte. In general, it is found that the smaller the analytically determinable adsorption the greater the charging of the diaphragm. J. F. S.

The Construction of Platinum Resistance Thermometers and Immersion Heating Coils of Low Lag. T. S. SLIGH, JUN. (*J. Amer. Chem. Soc.*, 1921, **43**, 470—475).—Improvements in constructional detail in the platinum resistance thermometers described in Bureau of Standards Bulletin, 1909, **6**, 150, and 1913, **9**, 483, are outlined. There is also described a convenient type of laboratory heating coil of low lag, specially suited for use as a bath thermo-regulator or for work involving the accurate measurement of heat supplied electrically. The heating coil is constructed by winding resistance ribbon on a flat strip of mica, insulating by means of thin mica side plates and enclosing in a flattened copper tube or sheath. [See *J. Soc. Chem. Ind.*, 1921, 326A.] E. H. R.

Calculation of the Specific Heats of Gases. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 125).—Three equations are deduced for calculating $C_p - C_v$, the difference between the specific heats of a gas at constant pressure and constant volume. These are (1) $C_p - C_v = 0{\cdot}000087/d_k v_k$, where d_k and v_k are the critical density and volume respectively; (2) $C_p - C_v = 0{\cdot}0935L/T_s$, where L is the heat of vaporisation at the boiling point T_s; (3) since $L = p_k T_s/T_k d_k$ (A., 1919, ii, 494), it follows that

$$C_p - C_v = 0{\cdot}0935 p_k/T_k d_k.$$

The formulæ are applied in a number of typical cases.

E. H. R.

Molecular Energy in Gases. (SIR) J. A. EWING (*Proc. Roy. Soc. Edin.*, 1920, **40**, 102—111).—The known facts with regard to the specific heat of gases from $-200°$ to $2000°$ have been reviewed and the following conclusions drawn. The increase in specific heat observed in most gases when heated is due to the setting up of to-and-fro vibrations of the atoms composing the molecules. The principle of equipartition does not apply to these

vibrations. In monatomic gases, substantially all the energy, so far as that is communicable, consists of energy of translation. Accordingly, the specific heat is sensibly constant, C_v having the value $\frac{3}{2}R$ and γ the value $\frac{5}{3}$. In diatomic gases, under normal conditions, the energy consists mainly of energy of translation and energy of rotation about axes transverse to the line joining the two atoms. The specific heat, C_v, is approximately $\frac{5}{2}R$, and $\frac{2}{5}$ of this quantity is accounted for by there being two (and only two) effective degrees of freedom of rotation. The normal value of γ is accordingly $1\frac{2}{5}$. When the gas is cold, the energy of vibration is nearly negligible, except in certain gases such as vapours of the halogens, where it forms an appreciable part of the whole energy even at ordinary temperatures. When a diatomic gas is heated, the to-and-fro vibration of the atoms comes increasingly into play and contributes a substantial addition to the energy, with the result that the specific heat rises and γ falls below $1\frac{2}{5}$. In all gases at all temperatures there is an equipartition of energy between each degree of freedom of translation and each effective degree of freedom of rotation. The abnormal behaviour of hydrogen at very low temperatures discovered by Eucken (A., 1912, ii, 232) may conjecturally be accounted for by supposing a change of molecular structure to occur which deprives the hydrogen molecule of its two normal degrees of freedom of rotation. If such a change of structure occurs it may be expected to exhibit hysteresis in relation to the temperature. In triatomic and polyatomic gases, there are three effective degrees of freedom of rotation which, along with the three degrees of freedom of translation, would make C_v equal to $3R$ and γ equal to $1\frac{1}{3}$ if there were no energy of vibration. But, in addition, there is in general a considerable amount of energy of vibration, resulting from to-and-fro movements of the atoms within the molecules, to which the principle of equipartition does not apply. Vibrations of relatively long period become important at relatively low temperatures. This makes the specific heat actually greater than $3R$ and γ less than $1\frac{1}{3}$, especially at high temperatures, when the energy of vibration becomes a large part of the whole energy. It does not appear to be necessary to have recourse to the quantum theory in dealing with molecular rotations in gases; at the same time, the observed facts do not conflict with the theory. The general effect of to-and-fro vibrations of atoms within the molecule of a gas is satisfactorily expressed in terms of the quantum theory. The resemblance which exists between the type of curve given by Planck's theory and the curve of magnetisation of a ferromagnetic substance suggests that if the nature of the atoms and their constraints were better understood the results might admit of interpretation in terms which would not be inconsistent with the older dynamics. J. F. S.

Specific Heat and Inner Atomic Vibrations. Franz Skaupy (*Zeitsch. Physik*, 1921, **4**, 100—104).—A critical discussion of the specific heat of compounds in connexion with the specific heat of the constituent elements. In order to bring the observed facts into line with the newer theory of atomic structure, the author

makes the assumption that the vibrations which chiefly condition the energy content of a solid substance are vibrations of the atomic parts, either the atomic nucleus and the whole electron sheath, or a part of the electron sheath and the residue of the atom. This vibration is characteristic of the atom, except in so far as it is influenced by the surrounding atoms. J. F. S.

Thermodynamics of Mixtures. V. MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1921, **97**, 229—252. Compare this vol., ii, 162).—A mathematical paper in which the material previously published is further discussed and extended. The Dolezalek theory of binary mixtures and concentrated solutions is discussed and its position with regard to experimental data indicated (A., 1909, ii, 22).
J. F. S.

Surface Tension and Heat of Vaporisation. W. HERZ *Zeitsch. Elektrochem.*, 1921, **27**, 25).—By combining the Trouton law with the Eötvös surface tension expression, the author has developed an expression connecting the surface tension with the heat of vaporisation. This has the form $L = 20\gamma/S^{2/3}M^{1/3}$, in which L is the heat of vaporisation, M the molecular weight, γ the surface tension at the boiling point, and s the density at the boiling point. The expression only holds approximately for normal liquids and not at all for associated liquids. From this formula the further expression $\rho = 1/10(M/s)^{1/3} . 0{\cdot}00102/42700$, in which ρ is the molecular diameter, is deduced. Using this formula, the diameter of the benzene molecule is found to be $1{\cdot}1 \times 10^{-8}$, which is of the same order as the value found by other methods. Combining the first equation with the expression $B = L/2v$, in which B is the internal pressure, this factor can be calculated by the formula $B = 10\gamma/(Mv)^{1/3} \times 42700/1033$, in which Mv is the molecular volume. The following values are calculated: benzene, 1830 atm.; ethyl acetate, 1425 atm.; and aniline, 2120 atm. J. F. S.

Heat of Vaporisation and Critical Data. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 26).—The author has deduced a second formula whereby the heat of vaporisation of non-associated liquids may be calculated from a knowledge of the critical data (compare A., 1919, ii, 494). The expression has the form $L = 0{\cdot}00093T_s/d_kv_k$, where L is the latent heat of vaporisation, T_s the absolute boiling point, and d_k and v_k the critical density and volume respectively. Since the Trouton rule $ML/T_s =$ constant, it follows that $M . 0{\cdot}00093/d_kv_k$ must also be constant. The two formulæ are tested for a number of non-associated liquids and found approximately to represent the facts. J. F. S.

Calculation of the van der Waals's Constants *a* and *b*. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 26—27).—Making use of expressions previously deduced (preceding abstract; A., 1919, ii, 494), the author has evolved three equations by means of which the constant b may be calculated. These have the form: (1) $b = T_s/2184L . d_k$, (ii) $b = v_k/2031$, and (iii) $b = 0{\cdot}0000216M/d_k$,

where the symbols have the significance given in the preceding abstract. The value of b is calculated for twelve substances by all three formulæ, and slightly divergent values are obtained. These are compared with the experimental figures, which are found to agree moderately well with some of the calculated values, although it cannot be said that any one of the formulæ is superior to the others. Two expressions for the calculation of a are also given, (i) $a = 6{\cdot}54 p_k v_k^2$ and (ii) $a = 1{\cdot}26 \times 10^8 p_k (M/d_k)^2$; again only a moderate agreement between the experimental and calculated values is obtained. Combining the last two formulæ, the relationship $v_k = 0{\cdot}0000439 M/d_k$ is obtained which connects the critical volume, critical density, and the molecular weight. J. F. S.

Vapour Pressure Regularities. IV and V. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 125—126. Compare A., 1920, ii, 163).—IV. If in van der Waals's equation the critical temperature is replaced by the expression $\frac{1}{2}(1/K_{20} + 293)$, where K_{20} is the co-efficient of expansion at 20°, the value of the factor a is close to, generally greater than, 3 for a number of liquids quoted, chiefly organic esters. In addition, the factor p_k (critical pressure) in van der Waals's equation can be replaced by the quantity $1/K_{20} + 293/0{\cdot}88n$, where n is the sum of the valencies of the constituent atoms. The value of a is thus calculated for a number of non-associated organic liquids.

V. The constant of Cederberg's vapour pressure formula (Thermodynamische Berechnung chemischer Affinitäten, p. 55, Upsala, 1916) when this is applied to organic compounds has an abnormally high value, increasing with the molecular weight of the compound. E. H. R.

Separation of Miscible Liquids by Distillation. A. F. DUFTON (*Phil. Mag.*, 1921, [vi], **41**, 633—646).—The separation of unit mass of a constituent A of a binary mixture of A and B involves the evaporation of a mass $1 + 1/a(k - 1)$ of the liquid, where a is the relative proportion of A in the liquid and $k = V_a L_b / V_b L_a$, where V_a, V_b are the masses of A and B in the vapour, and L_a, L_b the masses in the liquid. If Q is the latent heat of evaporation of the liquid, the quantity of heat required to separate unit mass of A is $Q\,[1 + 1/a(k - 1)]$. The ratio of the mass of A separated by this amount of heat to unit mass is called the thermal efficiency of the still-head. Mixtures of benzene and toluene were investigated with the Dufton still-head (A., 1919, ii, 136). With slower rates of heating the greatest thermal efficiency was obtained when the distillation was at the maximum rate to yield pure benzene. The thermal efficiency is reduced if loss of heat in the column is unduly prevented. J. R. P.

Heat of Sublimation of Carbon. H. KOHN (*Zeitsch. Physik*, 1920, **3**, 143—156).—It is shown that the temperature curve of the positive crater of a carbon arc, burning under pressures above atmospheric, can be regarded as the vapour pressure curve of carbon when pure carbon poles are used for the arc. This has been pre-

viously shown to be true also for reduced pressures (Fajans, *ibid.*, 1920, 1, 100—118). The calculation of the heat of sublimation made by Fajans is incorrect, owing to the use of inaccurate temperature values given by Lummer (Verflüssigung der Kohle Braunschweig, 1914). These temperatures have been corrected in the present work, and it is shown that the heat of sublimation of carbon, calculated from measurements over a pressure range 0·3—8·0 atm. which corresponds with a temperature range 4200—4700° abs., is 163·5 Cal. The heat of sublimation of the diamond therefore becomes 168 Cal., a value which approximates very nearly to the figure 142 Cal. which is obtained from the integrated vapour pressure formula by introducing the chemical constant for monatomic gases.

J. F. S.

The Thermochemical Data of Cadmium Chloride and Iodide. HUGH STOTT TAYLOR and GEORGE ST. JOHN PERROTT (*J. Amer. Chem. Soc.*, 1921, **43**, 484—493).—The *E.M.F.* and their temperature coefficients have been determined for the following cells.

Cadmium amalgam | $CdCl_2,2·5H_2O$ and saturated solution | AgCl | Ag, 0·62478 volt at 25°; 0·6249 volt at 0°.

Cadmium amalgam | $CdCl_2,2·5H_2O$ and saturated solution | $PbCl_2$ | lead amalgam, 0·1484 volt at 25° and 0°.

Cadmium amalgam | CdI_2 and saturated solution | AgI | Ag, 0·305 volt at 40°, 0·3035 volt at 25°, 0·3006 volt at 0°.

Cadmium amalgam | CdI_2 and saturated solution | PbI_2 | lead amalgam, 0·1135 at 40°, 0·10725 at 25°, 0·09655 volt at 0°.

Values for the heat of formation of cadmium chloride and of cadmium iodide from their elementary constituents were calculated from the electrical measurements. In the case of cadmium chloride it is deduced that a value of 93,000 cal., obtained from the electrical measurements, is more trustworthy than Thomsen's value from thermochemical measurements. Calculations of the heat of formation of cadmium iodide from different electrical data gave somewhat discordant results. This constant was therefore redetermined by direct measurement of the heat of formation, by dropping iodine into a solution of potassium iodide containing finely divided cadmium in suspension. The value found was 48,440 cal. and, combining the values determined directly and electrically, it is concluded that the most probable value is about 48,500 cal.

E. H. R.

The Elementary Quantity of Energy Brought into Action in Solution. RENÉ AUDUBERT (*Compt. rend.*, 1921, **172**, 676—678).—On the basis that solution and vaporisation obey the same laws, the value of ρ/T, where ρ is the molecular latent heat of solution and T the temperature which corresponds, for a state of saturation, to an osmotic pressure of one atmosphere, should be a constant. It is not possible to verify this directly, but by extrapolation from known results in the case of a number of salts the value of ρ/T is found to be 30—32, for $\pi = 1$ atm. From this the elementary quantity of energy necessary to cause a molecule

to pass into solution is calculated to be $18 \times 10^{-16}\, T$ ergs, which is the value found for the energy of dissociation of solids and for the energy of sublimation. W. G.

Surface Tension of Mercury in a Vacuum. JULIO PALACIOS (*Anal. Fís. Quím.*, 1920, **18**, 294—307).—Using a specially devised apparatus and mercury the freedom of which from impurities was verified spectroscopically, the author obtains the value 402 dynes/centimetre for the surface tension of mercury. This result is considerably lower than the values obtained by earlier workers.
G. W. R.

Interfacial Tension. I. The Statical Measurement of Interfacial Tension in Absolute Units. WILLIAM COLEBROOK REYNOLDS (T., 1921, **119**, 460—465).

Interfacial Tension. II. The Relation between Interfacial and Surface Tension in Sundry Organic Solvents in Contact with Aqueous Solutions. WILLIAM COLEBROOK REYNOLDS (T., 1921, **119**, 466—476).

The Adsorption of Alkali Chlorides by Animal Charcoal. HANS HARTLEBEN (*Biochem. Zeitsch.*, 1921, **115**, 46—51).—All alkali chlorides are adsorbed by animal charcoal within the limits of experimental error to the same extent. S. S. Z.

Adsorption of Formaldehyde by Animal Charcoal. W. MOELLER (*Kolloid Zeitsch.*, 1921, **28**, 127—132).—The adsorption of formaldehyde by animal charcoal has been examined in both acid and neutral solution. The adsorption in both cases is very great and follows the adsorption laws; that is, the adsorption is dependent on the concentration. The adsorption of formaldehyde by animal charcoal in acid solution is dependent on the volume in the sense that a great deal more is adsorbed from a large volume than from a small volume of equal concentration. In neutral solution the adsorption is independent of the volume and is practically dependent on the total quantity of formaldehyde present. In neutral solution the adsorption is independent of the time, and equilibrium is set up in a very short time. The adsorption from acid solutions is dependent on the time and equilibrium is set up very slowly, so that even after eight days' contact no equilibrium has been reached. J. F. S.

The Determination of the Sorption of both Solvent and Solute. I. Preliminary. The System: Benzene–Iodine–Charcoal. ABU MOHAMED BAKR and JOSEPH EDGAR KING (T., 1921, **119**, 454—460).

Explanation of an Apparent Anomaly outstanding in the Results of Measurement of Dissociation Pressures. ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1920, **40**, 158—160. See A., 1920, ii, 412).

The Dissociation Pressures of Iron Nitrides. ARTHUR A. NOYES and LEIGHTON B. SMITH (*J. Amer. Chem. Soc.*, 1921, **43**, 475—481).—Iron nitride is readily formed at 460° by the action

of ammonia gas on iron. If the equilibrium constant of this reaction in its general form $2Fe_xN + 3H_2 = 2_xFe + 2NH_3$ be expressed by K_1, and that of the reaction $N_2 + 3H_2 = 2NH_3$ by K_2, it is shown that the dissociation pressure of iron nitride can be expressed by K_1/K_2. The value of K_2 at 460°, calculated from known data, is $5{\cdot}10 \times 10^{-5}$; that of K_1 has been determined by the authors. The method consisted in admitting ammonia or hydrogen to the reaction tube containing iron and iron nitride and, after a period of fifteen to thirty minutes, suddenly withdrawing and cooling a quantity of the gas and analysing it. The experiments were made at 460°, and the time was chosen to allow the first above reaction to come to equilibrium before slower reactions could cause complications. The ratio Fe : N in the solid phase was varied between 17·1 and 2·59. When this ratio was greater than 9, the equilibrium constant $K_1=(P_{NH_3})^2/(P_{H_2})^3$ remained at 0·8 to 1·2, indicating probably the existence of a stable nitride, Fe_8N. When the Fe : N ratio became 7·7, the constant became 5·2 and increased to 30 with Fe : N = 4·9 : 1. Finally with Fe : N = 2·6 : 1 the value of K_1 fell again to 2·1. These stages may correspond with the formation of a metastable nitride such as Fe_4N in solid solution with the first, Fe_8N, or of two metastable nitrides such as Fe_6N and Fe_4N as separate solid phases; and finally of a stable nitride, probably Fe_2N.

The dissociation pressures of the nitrides in the above solid phases were calculated from K_1/K_2 and were found to be 20,000, 102,000, 590,000, and 41,000 atmospheres respectively. The work affords an example of the possibility of determining, through the study of a metastable equilibrium, the equilibrium conditions of a reaction not directly accessible to measurement. If, in the above reaction, complete equilibrium were established, all but about 0·1% of the ammonia would be dissociated and the iron nitride, with its high dissociation pressure, would not form at all.

E. H. R.

Solubility. I. FRITZ EPHRAIM (*Ber.*, 1921, **54**, [*B*], 379—385).—Solubility is defined as a type of miscibility, and it is pointed out that the latter phenomenon is invariably encountered with substances which are closely allied chemically. The solubility of salts in water depends on the ability of their molecules or ions to surround themselves with a water mantle and thus to approximate in character to the solvent. Since the author's researches (A., 1918, i, 389; 1920, ii, 378) have shown that the additive capacity of compounds is greatly dependent on spatial relationships, it would be expected that, if this factor is connected with the solubility, the latter would also be greatly dependent on the structure of the molecule. If a molecule is composed of a small kation surrounded by several very large anions, a hollow exists around the former which can be filled by neutral portions; if these are water, the whole molecule becomes water-like and therefore soluble. Sparing solubility is encountered with salts with spatially similar anions and kations.

The ideas which are thus developed are applied to the examination

of several cases in which addition of water is unlikely by reason of the presence of other neutral portions, as with the cobaltammines, or of the absence of any tendency to unite with water as in the case of the benzene or naphthalene ring. Comparable spatial relationships are encountered with the salts of the alkaloids and those of positive complex cobaltammines, and it is found (for details see this vol., ii, 338) that all the known precipitants for alkaloids also yield precipitates with the *leuco*-cobalti-compounds, $[Co(NH_3)_6]X_3$, and that the compounds thus formed are so similar that they would be scarcely distinguishable by eye from one another if the cobalt derivatives did not impart certain colorations. Conversely, many cobaltammines give precipitates with the complex anion, $\left[Co\begin{matrix}(NH_3)_2\\(NO_2)_4\end{matrix}\right]$, and precisely similar precipitates are now found to be given by alkaloids with this reagent. These reactions do not depend on the highly complex character of the cobaltammines, since they are also exhibited by the relatively less complex ammines of bivalent metals. Salts composed of small kations and a very large anion are generally freely soluble, but can be rendered insoluble when the two parts are spatially matched by the addition of neutral portions to the kation. Thus the picrates of small kations are freely soluble, but those of the ammines of small kations are sparingly soluble (following abstracts).

A second possible factor governing the solubility of salts is their tendency towards isomerisation. Thus Hantzsch (A., 1918, i, 4) has shown that the esters and salts of an acid frequently exhibit very divergent optical behaviour, whilst that of the acid itself lies between the two extremes. This is accounted for by the supposition that the alkyl group of the ester is attached exclusively to one oxygen atom, R·CO·OAlk, whilst the metallic atom of the salt may be related to two oxygen atoms, $R\cdot C\!\!<\!\!\begin{matrix}O\\O\end{matrix}\!\!\Big\}X$, the acid being a mixture of the forms $R\cdot CO\cdot OH \rightleftharpoons R\cdot C\!\!<\!\!\begin{matrix}O\\O\end{matrix}\!\!\Big\}H$. These investigations are based on observations on dissolved substances, but it appears justifiable to conclude that the undissolved salt can also contain the ester form, R·CO·OX, and that this is particularly the case with many sparingly soluble salts; the hydratisation of the metal would certainly be more difficult in the "ester" than in the "salt" form, since it is to a certain extent in complex combination. Observations on benzoates (compare A., 1918, i, 389) indicate the possibility of the existence of both types, since a solution of sodium benzoate only slowly yields a precipitate with salts of certain heavy metals such as nickel, cobalt, manganese, or bivalent iron, which is almost colourless, whereas the other salts of these metals are in general coloured and the mother liquors retain the colour of the metallic salt solution. The co-ordination form $\left[R\cdot C\begin{matrix}:O_2\\ \cdot X\end{matrix}\right]$ appears to be even more probable for the insoluble salts than the ester form.

Sparingly soluble salts of the ionisable type are also found in

which anion and kation are so spatially adapted to one another that the addition of water molecules is exceedingly difficult, ($K_2PtCl_6,KClO_4$). A fundamental difference, however, exists between the sparing solubility of salts of the ester type and ionisable type in that in the former case there is practically no chance of solubility in this form, whilst in the latter less or greater solubility is always present. H. W.

Solubility. VI. Thermodynamic Relation between Solubility and Internal Pressure. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1921, **43**, 500—507).—In the case of a binary liquid mixture it is shown by a process of thermodynamic reasoning that, if Raoult's law holds, the two liquids mix without any heat effect and without volume change. It follows from this that only such liquids as have identical values of $(\partial P/\partial T)_V$, that is, the same rate of change of pressure with temperature at constant volume, are capable of yielding solutions obeying Raoult's law under all conditions, that is, at all temperatures, pressures, and compositions. The above term is seen to be related to the equation of state $P + (\partial E/\partial V)_T = T(\partial P/\partial T)_V$, where E denotes total energy. It is proposed to define "internal pressure" as $T(\partial P/\partial T)_V$, which is practically equal to $(\partial E/\partial V)_T$, since P is small in comparison with the other terms. Defined in this way, internal pressure is capable of accurate measurement, since $(\partial P/\partial T)_V = -(\partial P/\partial V)_T(\partial V/\partial T)_P = \alpha/\beta$, where α, the coefficient of expansion, is $(\partial V/\partial T)_P/V$ and β, the compressibility, is $-(\partial V/\partial P)_T/V$. The values for the internal pressure of a number of liquids are calculated in this way.

Since the internal pressure of a solution of non-polar liquids is probably a linear function of the composition expressed in mol-fractions, it is probable that the difference between the internal pressures of the two pure liquids would determine, at least to a considerable extent, the deviation of the solution from Raoult's law. The relation between surface tension and internal pressure is discussed. It is shown that the criteria previously used for estimating relative values of internal pressure are in substantial accord with the thermodynamic definition of internal pressure now proposed, although it is theoretically preferable to use surface energy in place of surface tension (compare A., 1918, ii, 36). E. H. R.

The Miscibility of Liquids. CHARLES E. FAWSITT and CHRISTIAN H. FISCHER (*J. Roy. Soc. New South Wales*, 1919, **53**, 162—165).—A table of organic liquid substances was drawn up by Holmes (T., 1913, **103**, 2147) in which the liquids were arranged in the order of the radii of their molecular volumes (assuming the molecules to be spherical) starting with water, and it was shown that this table constituted, in fact, a miscibility table. The authors have drawn up an extended table, from experiments with the different substances, comprising 55 liquids, arranged in such an order that, if any two of them are miscible, then all the liquids between these two are perfectly miscible. The order of the liquids differs slightly from that in Holmes's table. Replace-

ment of hydrogen in a hydrocarbon by $\cdot OH$, $\cdot CO_2H$, $\cdot C_2H_3O_2$, or $\cdot NH_2$ brings the liquid nearer the beginning of the table, whilst replacement of hydrogen by $\cdot CH_3$ moves it in the opposite direction. Unsaturated hydrocarbons are nearer the beginning of the table than the corresponding saturated hydrocarbons. E. H. R.

Volume Changes in the Process of Solution. GEORGE JOSEPH BURROWS (*J. Roy. Soc. New South Wales*, 1919, **53**, 74—99). —The specific or molecular solution volume of any solute is generally calculated on the assumption that the volume of the solvent is unaltered by the process of solution, any change in volume of the system being attributed to the solute. The solution volumes of the following substances in water at different concentrations were determined on this assumption from measurements of the densities of the different solutions at 25° or 30°: potassium chloride, mercuric chloride, saccharamide, succinic acid, succinamide, tricarballylamide, carbamide, acetamide, propionamide, and sucrose. In most cases the solution volume was found to increase with concentration, the change being most marked with electrolytes, but in the cases of mercuric chloride and acetamide the solution volume decreased with increasing concentration. It is pointed out, however, that these changes in specific solution volume of the solute are only apparent and must be in some measure due to changes in the volume of the solvent. In some cases, for instance in dilute solutions of magnesium sulphate, the volume of the solution is actually less than the volume of water present. Measurements were made of the density of solutions of formamide in water over the complete range from 0% to 100% of formamide, regarding the formamide as the solute. The solution volume of the formamide steadily increased with increasing concentration, whereas the relative contraction of the system actually increased from 0% to 44% formamide and then decreased. Similar results were obtained with solutions of ethyl alcohol in water. The volume changes cannot therefore be attributed to the solute alone.

The molecular solution volumes determined for the above organic substances, which do not vary to any great extent with concentration, agree closely with the values calculated from Traube's atomic solution volumes and co-volume (A., 1895, ii, 70; 1896, ii, 152, 354).

The molecular solution volumes of the amides of the fatty acids from formic to hexoic were determined in ethyl alcohol at 30° and were found to be independent of concentration. The difference between the volumes of consecutive members of the homologous series was constant at 16·8 up to butyramide, but for higher members the difference increased.

A study was also made of solution volumes in mixtures of solvents of varying composition. The value of the solution volume of benzophenone in mixtures of acetone and benzene was intermediate between the values in the pure solvents, but in acetone–ethyl alcohol mixtures the value was identical with that in the alcohol alone. Carbamide, formamide, acetamide, propionamide, and sucrose were

examined in water–alcohol mixtures and in every case the specific solution volume in the mixture was greater than in either solvent alone. In the case of formamide the solution volume in the mixed solvent was actually greater than the specific volume of the pure liquid solute. In each case a maximum value for the solution volume of the solute was found at a certain composition of the mixed solvent, but the position of this maximum varied with different solutes. The author rejects the solvate theory, and considers that the volume changes which occur on mixing liquids or on dissolving substances in simple solvents or mixtures of solvents result from a rearrangement of the molecules in the system to admit of closer packing. E. H. R.

The Power of Solution and Ionisation of Non-aqueous Solvents toward Binary Salts. P. WALDEN (*Zeitsch. Elektro chem.*, 1921, **27**, 34—37).—A theoretical paper in which from previously published data the relationships between the solvent power and ionising power toward binary electrolytes are considered for a number of non-aqueous solvents. It is shown for the binary salt tetramethylammonium thiocyanate, which is a strong electrolyte, that at the saturation point the degree of ionisation is practically the same in all the solvents examined, $\alpha_1 = \alpha_2 \ldots\ldots = 0{\cdot}380$. The actual values given, where V is the number of litres of solvent containing one gram-molecule of tetramethylammonium thiocyanate and α is the degree of ionisation at 25° are: methyl alcohol, $V = 2{\cdot}18$, $\alpha = 0{\cdot}377$, nitromethane, $V = 3{\cdot}59$, $\alpha = 0{\cdot}385$; acetonitrile, $V = 4{\cdot}54$, $\alpha = 0{\cdot}379$; ethyl cyanoacetate, $V = 10{\cdot}95$, $\alpha = 0{\cdot}381$; propionitrile, $V = 20$, $\alpha = 0{\cdot}390$; acetone, $V = 37{\cdot}6$, $\alpha = 0{\cdot}369$; epichlorohydrin, $V = 27{\cdot}8$, $\alpha = 0{\cdot}388$; phenylacetonitrile, $V = 43{\cdot}7$, $\alpha = 0{\cdot}374$, and methyl ethyl ketone, $V = 98{\cdot}9$, $\alpha = 0{\cdot}381$. The solubility of the same salt is given by the expression $\epsilon/\mu^{\frac{1}{3}} \sim 34$ for different non-aqueous solvents when ϵ represents the dielectric constant and μ the molecular solubility. J. F. S.

Reactivity and Conductance of Benzene Solutions. H. P. CADY and E. J. BALDWIN (*J. Amer. Chem. Soc.*, 1921, **43**, 646—651).—According to Allen (*Kansas Univ. Sci. Bulletin*, 1905), and Cady, and Lichtenwalter (A., 1913, ii, 916), benzene solutions of salts of organic acids, which gave precipitates on treatment with dry hydrogen chloride, showed a conductivity in accordance with the dissociation hypothesis. The objection of Koenig (A., 1914, i, 653) that the salts in question were slightly basic has now been met by a study of copper oleate, barium erucate, copper stearate, and silver melissate, obtained from sodium salts in the preparation of which a slight excess of acid was employed. Solutions of these salts in benzene showed an appreciable conductivity, which was increased on passing in dry hydrogen chloride, but gradually diminished in the first two cases owing to formation of a precipitate. A similar result followed on the addition of a solution of stannic chloride in benzene to that of copper oleate (compare Koenig, *loc. cit.*). A solution of oleic acid in benzene was practically

non-conducting, and was only slightly affected in this respect by hydrogen chloride, but the addition of a stannic chloride solution gave rise to a considerable conductivity. J. K.

Electro-crystalline Properties as Conditioned by Atomic Lattices. (SIR) JOSEPH LARMOR (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 1—10).—The assumption that the crystal lattice consists of atoms (ions), not molecules, is considered with relation to the charges on the ions. It is shown that compensating surface charges on certain faces of crystals are required. Dielectric excitation is regarded as due to the relative displacement of the positive and negative component lattices under the influence of the electric field. If the lattice has spiral features this relative displacement may involve twisting, and optical rotation may be produced. The twisting is, in the case of quartz and optically active liquids, roughly comparable with the elongation. Double refraction induced by strain is attributed to bending of the ionic lattices or fragments of such lattices. J. R. P.

Ionic Size and Lattice Energy of the Alkali Haloids for Atom Models with Cubic Symmetry. HUGO SCHWENDENWEIN (*Zeitsch. Physik*, 1921, **4**, 73—88).—The lattice potential of the alkali haloids have been recalculated by means of the Rella formula (*ibid.*, 1920, **2**, 157) on the basis of the Landé cubic ring model (*ibid.*, 1920, **2**, 83). By means of the equilibrium conditions the ionic radii are then calculated whereby values are obtained which differ considerably from those given by Landé. If these values are used to calculate the lattice energy a series of quantities is obtained for the alkali haloids which are in very good agreement with those found from the heat of solution. The electron affinity values calculated for the various alkali haloids agree better amongst themselves than those obtained according to the original Born formula, but the compressibility of the crystals is too great. In general, the present calculations confirm the earlier calculations of Fajans and Herzfeld (*ibid.*, 1920, **2**, 309) made on the basis of the cube corner model. J. F. S.

Photometric Methods and Apparatus for the Study of Colloids. S. E. SHEPPARD and FELIX A. ELLIOTT (*J. Amer. Chem. Soc.*, 1921, **43**, 531—539).—Two types of photometer, distinguished as vertical and horizontal types, for the study of colloids, are described. The vertical type can be modified for use as a nephelometer, colorimeter, microphotometer, dispersimeter, or turbidimeter. The horizontal type is strictly a transmission and scatter photometer, and is useful for determining particle size, comparative turbidities, and coagulation velocities. For a full description of the apparatus, its mode of use, and a discussion of its limitations the original must be consulted. E. H. R.

The Zone of Maximum Colloidality. Its Relation to Viscosity in Hydrophile Colloids, especially Karaya Gum and Gelatin. JEROME ALEXANDER (*J. Amer. Chem. Soc.*, 1921, **43**, 434—440).—The viscosity of reversible emulsoid or hydrophile colloids sometimes

increases as the dispersed phase becomes finer, as in oil emulsions, for example, or sometimes as the dispersed phase becomes coarser, as in the case of soaps or butyric acid. There appears to be, in fact, a "zone of maximum colloidality," above which viscosity decreases with coarser subdivision, as the Brownian movement becomes sluggish, and below which it also decreases as molecular dimensions are approached. This zone will probably differ with different substances. The approach towards the zone of maximum colloidality from the side of coarse dispersion is illustrated by the clays, and from the side of molecular dispersion by the salts of the fatty acids. Experiments in which Karaya gum ground to different degrees of fineness was dispersed in water showed that the viscosity increased with increasing fineness of subdivision of the particles. Increase in viscosity accompanies the hydration and swelling of the particles, and as the dispersed phase becomes less viscous by swelling, the colloid as a whole becomes more viscous. The mechanism of the hydration process is discussed at some length and illustrated by the behaviour of the dried gum. The dehydration which occurs on drying appears to be accompanied by the removal of the protective aqueous films surrounding the micelles or their primary particles, in consequence of which the molecules or molecular groups approach one another so closely that the attraction of water or its ions is unable to separate them. The insolubility of heated gelatin is brought about in a similar manner. The decrease in the viscosity and jelly strength of highly degraded glue or gelatin probably does not represent a decrease in the dispersion, as has been suggested, but an increased dispersion, involving or followed by the formation of a small quantity of an insoluble or adsorption compound. E. H. R.

The Elastic Properties of Gelatin Jellies. S. E. SHEPPARD and S. S. SWEET (*J. Amer. Chem. Soc.*, 1921, **43**, 539—547).—Measurements of the modulus of rigidity of gelatin jellies, at different concentrations under torsion show that they follow Hooke's law nearly up to the breaking point, the elastic limit very nearly coinciding with the so-called tenacity (*J. Ind. Eng. Chem.*, 1920, **12**, 1007). The relation between the modulus of elasticity E and the concentration is expressed by $E = kc^n$ over a limited range, but the constants k and n differ for different grades of gelatin. Measurements of the effect of acidity on the elasticity showed that the latter is not a simple function of the hydrogen-ion concentration. The effect of the addition of alcohol is to increase the modulus of rigidity up to about 25% alcohol, after which the strength decreases. With above 40% alcohol, alcohol and water are squeezed out of the jelly under torsion, and the residual jelly becomes transparent and gives almost unlimited twist. Glycerol increases the jelly strength. The results indicate that gelatin jellies may represent any transition stage between two extreme types, one a two-phase type of structure with sub-microscopic period, the other a type in which mechanical strength must be attributed to solution forces, the system being physically homogeneous down to molecular or submolecular dimensions. E. H. R.

Protective Colloids. IX. Isinglass as Protective Colloid. I. Colloid Chemical Investigation of Isinglass. A. GUTBIER and P. BECKMANN (*Kolloid Zeitsch.*, 1921, **28**, 167—172).—Colloidal solutions have been prepared from isinglass, by digesting with water, chloroform water, and water to which a quantity of glycerol has been added. The sols thus produced have been subjected to ageing experiments in various concentrations. The viscosity of the solutions has been measured in various concentrations and at various periods after preparation. The influence of hydrochloric acid, potassium chloride, and sodium hydroxide has also been followed by the change in the viscosity brought about by these substances. The results show that the addition of these electrolytes does not bring about any fundamental change in the nature of the colloid. The viscosity data are all expressed in curves in the paper. J. F. S.

The Velocity of Flocculation of Selenium Sol. II. Flocculation by Means of Barium Chloride. H. R. KRUYT and A. E. VAN ARKEL (*Rec. trav. chim.*, 1921, **40**, 169—191. Compare A., 1920, ii, 739).—In the flocculation of selenium sol by barium chloride, it is again shown that von Smoluchowski's theory is not capable of entirely explaining slow flocculation. There is a wide range where it is verified, particularly for diluted sols, but there is a range where departures from the theory are observed, but in a contrary sense to those observed with potassium chloride (*loc. cit.*).

A series of measurements of cataphoresis was made with the selenium sol to determine the influence of electrolytes on the potential of the surface of contact. The results are examined and discussed in the light of Smoluchowski's theory and the observations of other workers, but no definite conclusion is drawn.

A comparison between gold and selenium sols is given, and the relationship between the potential of the limit surface, the concentration of the electrolyte, and the probability of adhesion are discussed. The departure from Smoluchowski's theory with respect to the duration of flocculation is observed to some slight extent with gold sols. W. G.

Coagulation and Solution of Silver Bromide Sols by Ammonia. RUDOLF AUERBACH (*Kolloid Zeitsch.*, 1921, **28**, 124—126).—The action of ammonia on silver bromide hydrosols has been examined by means of turbidity measurements, when it was found that coagulation and hydrolysis occur mutually in the same system. It is shown that in medium, but greater than equivalent, concentrations of ammonia the coagulation velocity at first predominates, but at higher concentrations the velocity of solution predominates. J. F. S.

Ultramicroscopic Structure of Soaps. W. F. DARKE, J. W. MCBAIN, and C. S. SALMON (*Proc. Roy. Soc.*, 1921, [*A*], **98**, 395—409).—The ultramicroscopic structure of soaps and the rapid changes which occur have been recorded and examined by the use of a cinematograph camera. The ultramicroscopic observations

of Zsigmondy and Bachmann (A., 1913, ii, 194) have been confirmed, interpreted, and extended. Their observations referred almost entirely to soap curds and not to gels or sols, for the latter usually exhibit in the ultramicroscope nothing but Brownian particles, and those only under definite conditions. Curds of sodium soaps consist of a felt of hydrated fibres enmeshing and in equilibrium with a soap sol or gel of definite concentration, the solubility rising rapidly with temperature. The individual fibres may be many centimetres long, but they are barely of microscopic diameter. Potassium soap solutions, on cooling, first develop fibres which are similar to those of the sodium soaps, except that they are only a few hundredths of a millimetre in length, and they have a strong tendency to form twins. The stable condition at the ordinary temperature is, however, the formation of innumerable tiny lamellar crystals of hydrated soap. The hydrogen soap, cetylsulphonic acid, is similar to the potassium soaps, but the particles of colloidal cetylsulphonic acid are very much more prominent. J. F. S.

Application of Statistics to Chemical Equilibria. K. F. HERZFELD (*Physikal. Zeitsch.*, 1921, **22**, 186—191).—A report on the modern work in connexion with the statistical method of treating chemical equilibria. The work is discussed in connexion with the classical theory, the quantum hypothesis, and charged systems. J. F. S.

The Properties of Diagrams. Curves Representative of the Displacement of the Equilibrium of Chemical Systems. JEAN BARBAUDY (*Compt. rend.*, 1921, **172**, 591—593).—A series of mathematical equations is deduced and their application to a consideration of the equilibrium in certain chemical systems discussed. W. G.

The Equilibrium between Nitric Oxide, Nitrogen Peroxide, and Aqueous Solution of Nitric Acid. CHARLES L. BURDICK and E. STANLEY FREED (*J. Amer. Chem. Soc.*, 1921, **43**, 518—530). —In the absorption by water of nitrous gases, such as are formed by the oxidation of ammonia, the reactions taking place are: (1) $2NO + O_2 = 2NO_2$; (2) $3NO_2 + H_2O = 2HNO_3 + NO$. The first of these reactions progresses slowly, whilst the second, although proceeding with great rapidity, comes to a stop at an equilibrium depending on the strength of the aqueous solution of nitric acid in which absorption is taking place and on the temperature. The equilibrium conditions of this second reaction have been studied by the determination of the partial constant $K_1 = (P_{NO})/(P_{NO_2})^3$ for nitric acid at different concentrations and temperatures. The experimental method used was to bubble nitrogen peroxide diluted with a large quantity of nitrogen through nitric acid at the required temperature and concentration and to determine the partial pressures of nitric oxide and nitrogen peroxide in the issuing gas. From measurements of the vapour pressures of water and nitric acid in nitric acid of different concentrations, the partial constant $(P_{HNO_3})^3/(P_{H_2O})$ was

also calculated. The experiments were limited to solutions containing between 10% and 55% of nitric acid, because with lower strengths the partial pressure of the nitrogen peroxide, and with higher strengths that of nitric oxide, was too small to measure. In order to obtain values of K_1 for more dilute solutions it was assumed that, for low concentrations, where K_1 approaches infinity, the reaction is complete. By means of vapour pressure data it was possible to extrapolate for concentrations of nitric acid above 55%. From the results obtained a table is given showing the percentage conversion of nitrogen peroxide into nitric acid by aqueous solutions containing from 5—65% of nitric acid at temperatures from 10—75°, for concentrations of nitrogen peroxide in the original gas varying from 0·1—20%. The favourable conditions for complete absorption are low temperature, dilute nitric acid, and high concentration of peroxide in the gas. With nitric acid stronger than 50%, absorption is very poor under all conditions.

From the above equilibrium and vapour pressure data, the free energies of nitric acid vapour and nitric acid in aqueous solutions were calculated. E. H. R.

Precipitation Equilibria. ROBERT GRIESSBACH (*Zeitsch. physikal. Chem.*, 1921, **97**, 22—94).—The equilibria set up in reactions of the type indicated by the equation aA_mS_n(solution) + bB_oR_p(solution) $\rightleftharpoons$ cA_qR_r(solid) + dB_sS_t (solution) have been investigated theoretically by treating the system as a trivariant three-phase equilibrium. The relationship between a given dependent and, at constant temperature, two independent concentrations can be expressed by a system of spacial co-ordinates :

$$\phi_1(N, C_1, C_2[C_3], \alpha, \beta, \gamma, x\, L) = 0,$$

where N is the quantity of solid phase per litre of solution (A_qR_r); positive when precipitated, negative when dissolved; C_1 the concentration of the salt to be precipitated (A_mS_n), C_2 the concentration of the precipitating salt (B_oR_p), C_3 the concentration of the salt B_sS_t should such be present before precipitation. α, β, γ, x are the reciprocals of the mass action constants for the four salts respectively, and L is the solubility product of the precipitate (A_qR_r). A second form of representation is more convenient, namely $\phi_{II}(\odot, C'_3\Delta) = 0$, in which $\odot = (C_1 - N)$ the solubility error of the determination, $C'_3 = (C_1 + C_3)$ the total quantity of neutral salt B_sS_t, from which, together with the excess of the solid phase and the excess of precipitant Δ the solution equilibrium can also be reached, $\Delta = C_2 - C_1$. Certain special assumptions concerning the variables lead to three elementary functions which correspond with definite plane intersections through the plane $\phi = 0$ and define the theoretical and experimental conditions of the equilibrium. $\phi = 0$ determines the influence on the sparingly soluble phase of the salts with a common ion (A_mS_n) and (B_oR_p). $\chi = 0$ indicates the influence of the salt with dissimilar ions (B_sS_t) on the solubility of the sparingly soluble phase, and $\psi = 0$ is the saturation curve of A_qR_r for the mutually precipitating salts (A_mS_n) and (B_oR_p). The introduction of one of the quantities C'_3, Δ, C_3

as parameter together with the above generalisations leads to the following $\phi\sigma'_3>0 = 0$; $\chi_{\Delta}>0 = 0$; $\psi\sigma'_3>0 = 0$. After making the usual simplifications the equilibrium scheme is calculated for the case AS(solution) + BR(solution) $\rightleftharpoons$ AR(solid) + BS(solution). The results obtained are then applied to experimental data. The experimental work of the present paper consists in the first place in the determination of the sources of error and then in the examination of the equilibria : $CH_3\cdot CO_2Na + AgNO_3 \rightleftharpoons CH_3\cdot CO_2Ag + NaNO_3$; $(CH_3\cdot CO_2)_2Ba + 2AgNO_3 \rightleftharpoons 2(CH_3\cdot CO_2)Ag + Ba(NO_3)_2$; $(CH_3\cdot CO_2)_3La + 3AgNO_3 \rightleftharpoons 3CH_3\cdot CO_2Ag + La(NO_3)_3$. The equilibria were reached in all cases from both sides, and it is shown that the experimental data confirm the theoretical curves obtained from the mathematical consideration. It is shown that the degree of subdivision of the solid phase is of first importance in determining the velocity and the sharpness with which the equilibrium is attained. The stability of silver acetate in contact with water and aqueous solutions depends on the purity of the salts used. The precipitation of barium sulphate in the presence of silver salts shows that the amount of silver salt occluded depends on the size of the particles of the precipitate, the velocity of precipitation, and the concentration of the silver salt. J. F. S.

Nature of Secondary Valence. II. Partition Coefficients. HOMER W. SMITH (*J. Physical Chem.*, 1921, **25**, 204—263; see this journal, ii, 324).—An empirical method of eliminating disturbing influences of dissociation, association, etc., in the distribution of a substance between two immiscible liquids is described. The partition coefficients of a large number of organic acids and bases between water and xylene and water and chloroform were determined. Attempts to connect these values with molecular volume are described. The observed points fall into several series, each of which is a straight line. These series are all parallel. The distances which separate several series are related to one another in a definite and periodic manner. J. R. P.

A Theory of Chemical Reactivity. Calculation of Rates of Reactions and Equilibrium Constants. SAUL DUSHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 397—433).—A theoretical paper in which a new theory of unimolecular reaction velocity is propounded after a critical discussion of the theories of Trautz, Lewis, and Langmuir. From the law of variation of reaction velocities with temperature, and from dimensional considerations, the velocity constant of a unimolecular reaction must be a frequency, and must satisfy a relation of the form $k_1 = \nu\epsilon^{-Q/RT}$ where ν is a frequency, $\epsilon^{-Q/RT}$ is the fraction of the molecules which are in the active state, and Q is the heat of activation. Assuming, with Lewis, that the process of activation is due to the absorption of radiation of a definite frequency, in quanta, it follows that the heat of activation per mol., $Q_A = Nh\nu_A$, where N is the number of molecules per mol., $= 6\cdot062 \times 10^{23}$, h is Planck's constant, and ν_A is the vibration frequency of the atoms. Now the frequency

ν above denotes the rate at which the active molecules decompose, and is probably related to the potential energy of the constituent atoms, that is, to the heat of activation. The author assumes that $\nu = \nu_A = Q_A/Nh$, and so arrives at the equation for the velocity constant of a unimolecular reaction $k_1 = Q_A/N_H \cdot \epsilon^{-Q_A/RT}$. By a simple transformation, introducing the known values of R, N, and h, this equation becomes $\log k_1 = 10{\cdot}0203 + \log Q_A - Q_A/4{\cdot}571T$. It follows that, from a single determination of the velocity constant at a given temperature it should be possible to calculate the heat of activation, or vice versa. This equation is tested against Trautz and Bhandarkar's figures for the dissociation of phosphorus hydride, PH_3, the only unimolecular reaction so far investigated which is free from the catalytic effect of the walls of the vessel, and the heat of activation found had a mean value of 72,750 cal. between 918° and 956° Abs. against 75,000 to 81,000 calculated from the temperature coefficient of k_1 by van't Hoff's equation (compare A., 1919, ii, 277).

For bimolecular reactions of the type $A + B \rightleftharpoons AB$, Jean's formula for calculating the frequency of collisions of active molecules is applied, and the following equation is deduced:

$$k_2 = N\sigma^2\sqrt{8\pi RT(1/M_A + 1/M_B)}, \ \epsilon^{-\frac{(Q_A+Q_B)}{RT}},$$

in which σ is the mean diameter of the molecules, M_A and M_B are the molecular weights of A and B, and $(Q_A + Q_B)$ the total heat of activation. This equation agrees well with experimental data for the reactions $H_2 + I_2 \rightleftharpoons 2HI$ and $2N_2O \longrightarrow 2N_2 + O_2$.

Equations are also deduced for several types of reversible reaction connecting the equilibrium constant K with the total heat of reaction Q. For example, for the reaction $A_2 + B_2 \rightleftharpoons 2AB$ the equation has the form $\log K = -Q/4{\cdot}57T + 0{\cdot}5 \log (M_{A_2} \,.\, M_{B_2})/4M^2_{AB}$. From the available data on homogeneous gas reactions, heats of reaction are calculated from these equations and agree, in a large proportion of cases, with the observed values.

In a discussion of heat of activation in dissociation reactions, it is shown, on general grounds, that the heat of activation must range between 40,000 and 100,000, and can be calculated approximately from the formula $\log Q_{AB} - Q_{AB}/4{\cdot}57T = -11$. It is generally assumed that in the reaction between activated atoms or molecules every collision is effective, but this may not always be the case, particularly with complex molecules, where steric factors may come into play. This may account for some of the discrepancies found between theory and experimental data.

It is concluded that the above equation for unimolecular reactions is of fundamental significance, although it does not lay claim to strict validity, but is probably influenced by at present unknown factors. The values calculated for the frequency term ν from the heat of activation correspond with a frequency in the visible or ultra-violet portion of the spectrum, supporting the conclusion that in chemical reactions the electrons play the fundamental rôle.

E. H. R.

Affinity of the Aragonite–Calcite Transformation. HANS L. J. BÄCKSTRÖM (*Zeitsch. physikal. Chem.*, 1921, **97**, 179—228).—The solubility of Iceland spar and synthetic aragonite in water in the presence of carbon dioxide of measured pressure (777—742 mm.) has been determined with an accuracy of 0·1% at 9°, 25°, and 35°. The values obtained for calcite were 1·30, 0·943, and 0·765 grams per litre at the three temperatures respectively, and for aragonite 1·46, 1·066, and 0·876 grams per litre respectively. The curves representing the reaching of equilibrium show, for Iceland spar at all temperatures and for aragonite at the lowest temperature, an unusual course, inasmuch as over a considerable portion the reaction velocity is practically zero. Powdered Iceland spar also shows a change with time, since the velocity of reaction in the course of the experiment gradually decreases. It is concluded that in the present case the Noyes-Nernst law, for the velocity of reaction in heterogeneous systems, does not hold. The heat of transition is calculated to − 670 cal. ± 100, whilst the directly determined value of Le Chatelier is − 600 cal. (A., 1893, ii, 259) and the transition point − 43° ± 5°. With increase in pressure, the transition point increases 1° per 40 atm. Hence pure aragonite can never constitute the stable phase in ordinary circumstances. Previous work on this subject is fully discussed. Compare Seyler and Lloyd (T., 1909, **95**, 1347), Bjerrum and Gjaldbæk (*Vet Landbohöjskole Aarskrift Kopenhagen*, 1919, 48), Foote (A., 1900, ii, 541), Kendall (A., 1916, ii, 512) and Warynski and Kouropatwinska (A., 1916, ii, 605). J. F. S.

Experimental Investigation of the Point of Inflammation and the Velocity of Reaction of a Hydrogen Oxygen Mixture. HERMANN FIESEL (*Zeitsch. physikal. Chem.*, 1921, **97**, 158—178).—The point of inflammation is defined as that temperature at which the velocity of reaction exceeds a measurable value. The point of inflammation of various mixtures of hydrogen and oxygen has been ascertained by bringing both gases to the required temperature and then mixing and ascertaining by means of a delicate membrane whether a pressure difference occurs and therefore whether rapid reaction has occurred. The minimum inflammation point lies at 397·5° for the mixture of hydrogen and oxygen ($3H_2 + 2O_2$); for equal volumes of the dry gases the value is 407°, and increases after the minimum to 433° for the mixture ($4H_2 + O_2$). In the case of acetylene–air mixtures, the inflammation point could be only approximately determined. It is shown that it is possible by the method described to determine the velocity coefficient (*kt*) of the absolute velocity of a gas reaction, provided that it takes place sufficiently rapidly and is exothermic. It is shown that the reaction between moist oxygen and hydrogen is bimolecular, and may proceed through hydrogen peroxide, whilst when absolutely dry gases are used the reaction is trimolecular. It is probable, but not actually established, that the apparent catalytic action of the water vapour depends mainly on a concentration change of the mixture, for it follows from the equation $v = kC_1^{n_1} \cdot C_2^{n_2}$ that if the concentration is changed by admixture with indifferent gas, the quantity v, and

therefore *kt*, must have a definite value for each temperature and the inflammation temperature will therefore be increased. A possibility of ascertaining the heat of formation of hydrogen peroxide by the present method of experiment is indicated. J. F. S.

The Influence of Copper on the Rate of Solution of Iron in Acids. FREDERICK K. BELL and WALTER A. PATRICK (*J. Amer. Chem. Soc.*, 1921, **43**, 452—465).—Experiments were made with alloys containing 0·1%, 0·3%, 0·5%, 1·0%, and 5% of copper to determine the effect of copper on the rate of solution of the iron in acids. The iron for the alloys was prepared by reduction of pure ferric oxide; the copper used was pure copper foil. On account of the slow rate of solution in dilute acids, the experiments were limited to more concentrated acids, 28·7% hydrochloric and 57·0% sulphuric acid. The experiments were carried out by exposing a polished surface of the metal to the action of the acid and measuring the rate of evolution of hydrogen. In hydrochloric acid, the rate of solution of the alloys showed a definite decrease in comparison with pure reduced iron, the first 0·5% of copper having the greatest effect, further increase in the copper content of the alloy only slightly increasing the resistance. It was found that mere contact with copper wire brings about a marked reduction in the rate of solution of pure reduced iron in hydrochloric acid, whilst platinum and silver are without effect. The results of the experiments in sulphuric acid were too erratic to be of any value. To explain the retarding effect of copper, it is suggested that a certain amount of copper passes into solution, and is at once reprecipitated in a finely divided state on the surface of the iron, to be redissolved by the acid. This intermittent solution and precipitation of the copper may be responsible for its retarding effect. E. H. R.

The Velocity of Hydration of Anhydrides of Dicarboxylic Acids. I. P. E. VERKADE (*Rec. trav. chim.*, 1921, **40**, 192—198).—In this introductory paper the author discusses various theories which have been proposed as to the hydration of anhydrides of dicarboxylic acids. He considers that it is possible that the hydration may take place in two stages, in the first of which the anhydride unites with water to form an additive product, which in the second stage may pass to the acid with a relatively greater velocity (compare A., 1916, ii, 234, 607). He urges the desirability of determining the velocities of hydration of a large number of anhydrides of dicarboxylic acids. W. G.

The Velocity of Hydration of Anhydrides of Dicarboxylic Acids. II. Methylated Succinic Anhydrides. P. E. VERKADE (*Rec. trav. chim.*, 1921, **40**, 199—221. Compare preceding abstract and Rivett and Sidgwick, T., 1910, **97**, 732, 1677).—The author has redetermined the velocity of hydration of the anhydrides of succinic acid and of the mono-, di-, tri-, and tetra-methylsuccinic acids and in most cases the dissociation constants of the acids. For *as*-dimethylsuccinic anhydride the value $0·4343k_{25} = 0·0762$ is given for the velocity of hydration; for trimethylsuccinic

anhydride $0{\cdot}4343k_{25} = 0{\cdot}0783$; and for tetramethylsuccinic anhydride $0{\cdot}4343k_{25} = 0{\cdot}00638$. W. G.

The Hydrolysis of Carbamide Hydrochloride. GEORGE JOSEPH BURROWS (*J. Roy. Soc. New South Wales*, 1919, **53**, 125—135).—The degree of hydrolysis of carbamide hydrochloride of different concentrations in mixtures of water and ethyl alcohol and water and acetone has been determined (compare Burrows and Fawsitt, T., 1914, **105**, 612). The determinations were made by measuring the rate of inversion of sucrose, first by hydrochloric acid alone in the mixed solvents, and then in presence of the required amount of carbamide, a correction for the influence of unhydrolysed hydrochloride being applied in the manner adopted by Walker and Wood (T., 1903, **83**, 484). In water–alcohol mixtures the degree of hydrolysis decreases with decreasing concentration of water. The hydrolysis constant H at 25° was calculated from the formula $H = h^2/(1 - h)_v$ where h is the degree of hydrolysis and v the volume in litres containing one gram-molecule of carbamide hydrochloride. The experiments at different concentrations indicate that in water–alcohol mixtures the effect of dilution may be expressed by the ordinary dilution law. The amount of hydrolysis depends on the concentration of salt in the total volume, and is not simply proportional to the amount of water present. In the case of acetone–water mixtures, however, the value of the hydrolysis constant is approximately proportional to the number of molecules of water in solution, the acetone apparently having no hydrolytic effect. E. H. R.

Time Factor in Saponification. PERCIVAL J. FRYER (*Analyst*, 1921, **46**, 87—90).—The velocity of the saponification of oils and fats, from the point of view of the amount of free alkali removed from the reacting solution, is in inverse ratio to the mean molecular weight of the fatty acids of the glycerides composing the natural oils and fats. In terms of the weight of oil or fat employed, results were obtained showing that all oils and fats, and probably all esters, are saponified at approximately equal rates under the same conditions. The velocity of saponification is very greatly influenced by small differences in temperature, and is increased in direct proportion to the molecular weight of the solvent employed; thus the velocity in ethyl alcohol is more than ten times that in methyl alcohol, and in amyl alcohol is about double that in ethyl alcohol. It is also increased by increase in the concentration of the alkali. W. P. S.

Kation Catalysis. IV. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1921, **97**, 134—157. Compare A., 1913, ii, 942).—It is assumed that the kation catalysis in a reaction between two strong electrolytes *MAR* and *MB* depends on the fact that the substance *MAR*, in which the reacting radicle constitutes only a portion of the corresponding anion, reacts more rapidly when un-ionised than when in the ionic condition, whilst the electrolyte *MB*, in which the anion is identical with the negatively charged reacting radicle,

reacts practically with equal rapidity as molecule and as ion. If α is the degree of ionisation of the first electrolyte, the formula $C = C_i\alpha + C_m(1 - \alpha)$ is obtained. To test this formula and the assumptions on which it is based, the velocity of the reaction between various thiocyanates and iodoacetic acid in neutral and acid solutions has been examined at 25°. It is shown that with a constant potassium concentration the reaction represented by the equation $CH_2I\cdot CO_2K + KSCN = SCN\cdot CH_2\cdot CO_2K + KI$ is a reaction of the second order. With increasing potassium concentration, the velocity constant is greater and may be represented by the formula $C = 2{\cdot}60[K]^{0{\cdot}197}$ and less well by the formula $C = 1{\cdot}24 + 4{\cdot}04[K]$. The experimental data are exactly reproduced by the expression $C = C_i\alpha + C_m(1 - \alpha)$, in which $C_i = 1{\cdot}12$, and $C_m = 4{\cdot}19$, corresponding with $k = 0{\cdot}04$. The values $k = 0{\cdot}6$, $C_i = 1{\cdot}15$, $C_m = 5{\cdot}04$, and $k = 0{\cdot}2$, $C_i = 1{\cdot}06$, and $C_m = 3{\cdot}32$ are also usable. In the case of sodium salts it is found that $C = 2{\cdot}46[\mathrm{Na}]^{0{\cdot}17} = 1{\cdot}35 + 2{\cdot}8[\mathrm{Na}] = 1{\cdot}12\alpha + 4{\cdot}25(1 - \alpha)$ for $k = 0{\cdot}4$ and for $k = 0{\cdot}2$, $C = 1{\cdot}06\alpha + 3{\cdot}30(1 - \alpha)$. Ammonium salts conform to the equation $C = 2{\cdot}66[NH_4]^{0{\cdot}167} = 1{\cdot}49 + 3{\cdot}0[NH_4] = 1{\cdot}12\alpha + 5{\cdot}16(1 - \alpha)$ for $k = 0{\cdot}4$ and for $k = 0{\cdot}2$, $C = 1{\cdot}06\alpha + 3{\cdot}92(1 - \alpha)$. Neither equation in the last case is particularly good. In the case of barium salts the equation $C = 3{\cdot}12[\mathrm{ba}]^{0{\cdot}181}$ was obtained. In solutions to which hydrochloric acid had been added the velocity constant is independent of the initial concentration and also of the concentration and nature of the metal kation. The constant found for the reaction between non-ionised iodo-acetic acid and the thiocyanate in any form is $C_{m(\mathrm{acid})} = 5{\cdot}72$. When free iodoacetic acid is used without the addition of hydrochloric acid, the velocity constant is also independent of the concentration and nature of the metal, but it increases with increasing initial concentration of the iodoacetic acid and can be calculated from the dissociation of the acid by the values $C_i = 1{\cdot}12$ and $C_{m(\mathrm{acid})} = 5{\cdot}72$. It is then found that the calculated C values are about 2% smaller than the experimental values; this is, however, explained by the fact that the thiocyanic acid produced is a stronger acid than iodoacetic acid and that the ionisation of this acid is therefore decreased and the velocity of reaction increased. A definite progression of the velocity coefficients was not obtained, but this was the case when one half of the iodoacetic acid was neutralised with potassium hydroxide. In general it is shown that the assumptions made are in keeping with the experimental data. J. F. S.

The Influencing of Catalysts, and Specifically Active Catalysts. KARL W. ROSENMUND and F. ZETZSCHE (*Ber.*, 1921, **54**, [*B*], 425—437).—In a previous communication (A., 1918, i, 300) the author has described the preparation of aldehydes by the reduction of acid chlorides dissolved in dry xylene or cumene with hydrogen in the presence of palladinised barium sulphate. The yields, although frequently very good, are nevertheless uncertain and a systematic study of the effect of adding small quantities of foreign materials to the solvent is now recorded. With pure benzoyl

chloride dissolved in pure boiling benzene, toluene, or cumene a scarcely weighable amount of benzaldehyde was produced; the effect of thiophen bromide, distilled or crude quinoline, quinoline boiled with one-sixth of its weight of sulphur under a reflux condenser for five to seven hours, thioquinanthrene, quinine, quinine hydroiodide, dimethylaniline, benzthiazine, phenylthiocarbimide, diphenyl disulphide, and the by-products from the preparation of the latter, was investigated, an increase in the yield of aldehyde being obtained in practically every instance and reaching its maximum in the case of "sulphured" quinoline. It is remarkable that reduction appears to stop at the aldehyde stage, instead of continuing to formation of the alcohol or hydrocarbon, and this seems to be the first case on record in which a specific catalyst has been artificially produced by the addition of a chemically well-defined substance. Under similar treatment, *o*-chlorobenzoyl chloride gives *o*-chlorobenzaldehyde, and *p*-nitrobenzoyl chloride is converted into *p*-nitrobenzaldehyde, the yields being more than 70% and 91% respectively. Phenylacetaldehyde is obtained in 80% yield from phenylacetyl chloride.

The mechanism of catalysis in general is fully discussed. The catalyst is assumed to react with all the components of the system, thereby forming a "complex" with a characteristic distribution of energy and molecules; this is a labile physical or chemical arrangement, for the decomposition of which the arrangement of forces with which the members of the "complex" act on one another, which is determined by the catalyst, is responsible. Catalysts can be influenced in their activity by sundry addenda in the direction (*a*) of the strengthening or weakening of the catalyst, thus giving the possibility of selective catalysis, and (*b*) the mode of action thus rendering possible selective action. The combination of (*a*) and (*b*) leads to the preparation of specific catalysts.

A substance which by itself is inactive or only feebly active can attain the properties of a catalyst after addition of other suitable substances. H. W.

Effect of Temperature on the Catalytic Power of Platinum and Palladium Sols. ANTONIO DE GREGORIO ROCASOLANO (*Anal. Fís. Quím.*, 1920, **18**, 308—317. Compare A., 1920, ii, 479, 607).—The decomposition of hydrogen peroxide by sols of platinum and palladium was studied at various temperatures. The decomposition curves showed a continuous increase of catalytic power up to the boiling points of the sols. This controverts earlier statements that the sols of these metals lose their catalytic power at their boiling points. According to the author, the catalytic activity of metallic sols resides in the metal–oxygen complexes, and as long as these are undecomposed, catalytic power is unaffected. Metallic dispersions are much more stable than organic dispersions, and up to the point of their decomposition their activity increases with temperature. G. W. R.

Twenty-seventh Annual Report of the Committee on Atomic Weights. Determinations Published during 1920. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1921, **43**, 383—390).

—Papers published during 1920 dealing with atomic weight determinations are summarised. E. H. R.

Spiral Classification of the Elements. L. BEAUMONT TANSLEY (*Chem. News*, 1921, **122**, 121—122).—Taking the atomic weight of uranium as centre, the elements are plotted radially, the 18 sub-groups being allotted 20° each of the complete circle. J. R. P.

A Law of Force giving Stability to the Rutherford Atom. J. MARSHALL (*Proc. Roy. Soc. Edin.*, 1920, **40**, 150—157).—A mathematical paper in which it is shown that if a law of force between a positive nucleus and a negative electron be of the form $1/r^2 - (b^{n-2}/r^{n-2})$ an n value can be found which will preserve the stability of a group of electrons, not exceeding seven in number, rotating round a positive nucleus in a circular orbit. Since b, a constant, is smaller than the radius of the atom, for distances large in comparison with the radius of the atom this law of force will differ from the inverse square law by a negligible quantity. Stability for the simple cases of the Rutherford atom will therefore be established. The question of the stability of a series of rings of electrons rotating about a positive nucleus introduces complexity into the rigorous analysis required. If the tentative assumption is made that, so far as the effect of an inner set of rings on the outer ring is concerned, they may be replaced by an equivalent charge at the centre of the atom, the conditions for the stability of an outer ring of p electrons rotating in a circular orbit will be determined by the equations $4p(1 - sk/p) > \sum_{t=1}^{p-1} \operatorname{cosec}^3 t\alpha \sin^2 kt\alpha$ and the reality of the roots of the equation $(F - q'^2)(G - q'^2) = (H - Jq')^2$, where $F = \sum_{t=1}^{p-1} \frac{1}{8}[5 \operatorname{cosec} t\alpha - \operatorname{cosec}^3 t\alpha + \cos tk\alpha(\operatorname{cosec} t\alpha + \operatorname{cosec}^3 t\alpha)] - p[3 - (n+1)sk/p]$; $J^2 = 4p(1 - sk/p) - \sum \operatorname{cosec} t\alpha$. In these conditions sk/p replaces k; and since $s > p$, the new value of k will be less than the previous value. This can be obtained, since r is greater for the outer set than for any one of the values of r for the inner set, the value of n being kept the same; or n may be increased as well as r and the increased value of n will still maintain the stability of the inner set. The displacements of the electrons in the outer ring perpendicular to the plane of the orbit will be unstable, however, when p exceeds seven. This would indicate that an atom could be built up of a series of rings of seven electrons, and a periodicity in the properties of the atoms corresponding with the periodic classification would be expected from such a structure. J. F. S.

State of Aggregation of the Elements and the Atom Model. F. A. HENGLEIN (*Zeitsch. Elektrochem.*, 1921, **27**, 28—30).—On the basis of the Stark theory of intramolecular and intermolecular linking together with the Kossel atomic model (Stark, "Prinzip. Atomdynamik," III., p. 3; Kossel, A., 1916, ii, 243), it is shown

that the state of aggregation of the elements may be simply represented. Thus the electrostatic force of attraction of the positive nucleus of an atom on its valency electrons increases in the horizontal series of the periodic system with increasing atomic number, and in the vertical groups decreases with increasing atomic number. The force of attraction of the atoms for one another increases in the same sense. In the first four groups of the periodic system this affects only the intramolecular linking, whereby the monatomic character of the elements results, and also, according to the strength of the force, their state of aggregation. In the fifth, sixth, and seventh groups, the forces lead to molecule formation, whereby some force is left over which leads to intermolecular linking and thereby the gaseous, liquid, and solid conditions of the elements are conditioned. In the case of the inactive gases, forces act from the positive nucleus on the valency electrons and produce a new configuration. The valency electrons are drawn by the strong force into the inner electron system, and since only feeble molecular forces are present these elements remain gaseous at very low temperatures. J. F. S.

Bohr's Model of the Atom and the Corpuscular Spectra. MAURICE DE BROGLIE and LOUIS DE BROGLIE (*Compt. rend.*, 1921, **172**, 746—748. Compare this vol., ii, 232).—A theoretical discussion of work previously published (*loc. cit.*). W. G.

Atomic Structure and Scattered Radiation. R. GLOCKER and M. KAUPP (*Ann. Physik*, 1921, **64**, 541—565).—Debye's formula (*Ann. Physik*, 1915, **46**, 809) for the intensity of radiation scattered by an atom containing a single electron ring is extended to atoms containing two or three rings. For long waves, the intensity of scattering is still proportional to the square of the total number of electrons in the atom. The carbon atom with six electrons may have one ring of 6 electrons, two rings of 2 and 4 electrons, or two rings of 3 and 3 electrons. The inner K-ring of 2 electrons corresponds with the position of carbon in the periodic system, but the K-ring of 3 electrons is required to give the correct position of the K_a line. Experimental results are shown to favour the inner ring of 2 electrons and outer ring of 4 electrons, although a tetrahedral arrangement of the 4 electrons gives the same result. A single ring of 6 electrons is not admissible. The 13 electrons of the aluminium atom may be divided among the three rings, beginning with the inner, in the proportions 2, 8, and 3, or 3, 9, and 1. Both cases satisfy the experimental results. The validity of Barkla's law for the scattering of radiation is called into question. J. R. P.

Atomic Nuclei. E. GEHRCKE (*Physikal. Zeitsch.*, 1921, **22**, 150—152).—On the basis of a slightly modified nitrogen nucleus (Rutherford, A., 1920, ii, 541), the author has put forward nuclei for carbon, oxygen, neon (20), neon (22), chlorine (35), chlorine (36), chlorine (37), chlorine (38), and chlorine (39). J. F. S.

Homochemical Compounds. P. P. von Weimarn (*Kolloid Zeitsch.*, 1921, **28**, 97—103).—A theoretical paper in which it is deduced that all atoms have a minimum valency of six, and when a given atom combines with less atoms of hydrogen or oxygen than this number demands, the fact is due to properties of the surface of the atom and to the strength of the linking in the hydrogen and oxygen doublets. It is also stated that every substance, under suitable conditions, is capable of forming homochemical compounds with every other substance which contains a similar atom or atomic grouping to that substance. J. F. S.

Nature of Secondary Valence. I. Homer W. Smith (*J. Physical Chem.*, 1921, **25**, 160—169).—Secondary valence is defined as the force which binds molecules together. Evidence is presented from a study of organic compounds to show that the views that secondary valence is due to stray force-fields or to attractions operating according to some mathematical power of the distance are erroneous. The forces acting between molecules are comparable to those forces in the atom which are responsible for atomic structure, in that they are rhythmic in nature and are not subject to ordinary electromagnetic laws. Every molecule behaves as though it completely fills a definite space which has a three-dimensional symmetry. It is stated that in any series of compounds having the same intrinsic intensity of secondary valence the partition coefficient is a simple logarithmic function of the molecular volume. J. R. P.

Active Cross-section of Gas Molecules for Slow Electrons. Carl Ramsauer (*Ann. Physik*, 1921, **64**, 513—540).—The active cross-sections of the molecules of various gases were determined by measurement of the absorption of slow (1 volt) electrons of definite speed and direction at low pressures. The following values in $cm.^2 \times 10^{-18}$ were found: hydrogen 1260; argon 75; nitrogen 920; helium 550; air 890. These values are the following multiples of those calculated from the kinetic theory: hydrogen 3·4; argon 0·14; nitrogen 1·4; helium 2·3; air 1·4. The results with argon were less certain than the others, hence the conclusion is drawn that an electron is either absorbed outright or is not influenced in any way as regards the magnitude and direction of its velocity by a gas molecule. There is for every atom or molecule a fixed sphere of action outside which a slow electron is not influenced, but inside which it is strongly influenced. That the action is one of rapidly diminishing distance action is improbable by reason of the constancy of section found with such an electrostatically "open" structure as hydrogen. The question as to whether the phenomenon is to be explained by a division of atomic energy into quanta or to a spatial discontinuity of the electromagnetic field is left open. J. R. P.

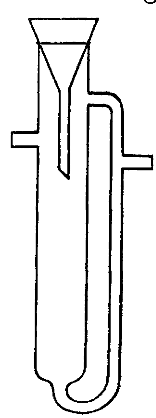
A New Method of Measuring Molecular Weights. J. G. Stephens (*J. Roy. Soc. New South Wales*, 1919, **53**, 166—170).—The method is based on the principle that, if two solutions containing different substances in solution in the same solvent are

together in a confined space, solvent will distil from one to the other until the vapour pressures are equal. When the vapour pressures are equal, the osmotic pressures are also equal, in other words, the molecular concentration is the same in each solution. The apparatus used consists of an inverted Y-tube; two test-tubes are ground into the two arms and the stem is provided with a stop-cock. In one test-tube is placed a known weight of a substance of known molecular weight in a known weight of solvent, and in the other a known weight of the substance the molecular weight of which is to be determined, also in a known weight of the same solvent. The apparatus is evacuated and allowed to remain until the weights of the two tubes have become constant. From the weight of solvent and solute in each tube the unknown molecular weight can then be calculated. Good results were obtained using benzene as solvent, but ethyl ether was not so satisfactory. E. H. R.

A Bunsen Burner Constructed from Glass Tubing. O. RUDOLPH (*Chem. Zeit.*, 1921, **45**, 289).—A burner giving a very small flame may be constructed from glass tubing by making a lateral opening, of the same diameter as that of the tube, in the lower part, for admission of air, and constricting the diameter of the tube below this opening to $\frac{3}{4}$ mm. for the gas passage. W. J. W.

Apparatus for Drying Substances which are Unstable at High Temperatures. O. RUDOLPH (*Chem. Zeit.*, 1921, **45**, 289).—An apparatus specially adapted for drying explosives or hygroscopic substances, consists essentially of a desiccator, which contains no desiccating agent; this is heated to the desired temperature in a water-bath, the air being at the same time nearly exhausted by means of a suction pump. A slow current of heated, dry air is then drawn into the apparatus through a leaden worm placed in the water-bath and leading into the desiccator through its tubulure, this worm being in communication with the calcium chloride drying tubes. The pressure maintained in the apparatus, as indicated by a manometer, should exceed the vapour tension, at the given temperature, of the vapour to be expelled by about 10 mm. The current of vapour-laden air passes out through a tube surrounding the inlet tube (or through a second tubulure if there be one) to absorption vessels. W. J. W.

The Automatic Separator in Esterifications and Other Preparations. I. N. HULTMAN, ANNE W. DAVIS, and H. T. CLARKE (*J. Amer. Chem. Soc.*, 1921, **43**, 366—370).—The separator is as sketched and forms a ready means of continuous separation of two immiscible liquids. If used in the distillation of a mixture of two such liquids, the distillate being collected in this apparatus, by suitable connexions it can be arranged that the heavier or lighter liquid, as desired, returns automatically to the distillation flask, whilst the other runs off to a receiver. Examples of its utility in various preparations are given. W. G.



Inorganic Chemistry.

Density of Hydrochloric Acid. J. FITCH KING (*J. Physical Chem.*, 1921, **25**, 115—121).—Discrepancies exist in published densities of 2*N*-hydrochloric acid. The value D_4^{15} 1·0344 was found. The concentration coefficient at this concentration, dD/dC, is 0·004986, and the temperature coefficient dD/dt is 0·000250.

J. R. P.

Preparation of Chlorine Heptoxide. FRIEDRICH MEYER and H. G. KESSLER (*Ber.*, 1921, **54**, 566—571).—A mixture of chlorine heptoxide and pyrosulphuryl chloride containing a little chlorine peroxide is obtained when a mixture of potassium perchlorate (3 parts) and chlorosulphonic acid (5 parts) is gradually heated to 70—75° in the vacuum of a water-pump; pale yellow chlorine heptoxide (98—99%) is prepared by the distillation of this product in a vacuum, but traces of sulphur compounds are obstinately retained even after repeated re-distillation. The process is almost without danger. Solutions of chlorine heptoxide in carbon tetrachloride are readily obtained by conducting the mixed gases obtained in the above process in succession into an empty receiver cooled to − 20° in which nearly all the pyrosulphuryl chloride condenses, and then into a second vessel, also cooled to − 20°, containing carbon tetrachloride, which dissolves the chlorine heptoxide and peroxide. The latter can be removed by gently boiling the solution and the residual liquid then retains only pyrosulphuryl chloride, chlorosulphonic acid, and sulphur trioxide as impurities, the total amount being 1—2% as a maximum.

Chlorine heptoxide in a higher state of purity can be obtained by the very cautious addition of phosphoric oxide to strongly-cooled perchloric acid (70%) in such a manner that the heptoxide can ultimately be distilled, but local overheating cannot be avoided and the yields are poor. The components can be safely brought together if previously absorbed by or mixed with purified and ignited kieselguhr or "K-silicic acid" (of the Elektro-Osmose Akt. Ges.); the adsorptive capacity of the material is such, however, that only a portion of the heptoxide is removed at about 80—90/0·2 mm. The yields are only about 10%, but the product is easily purified by distillation and the method is suitable when the substance is required in small quantity and high purity.

The preparation of pure solutions of chlorine heptoxide in carbon tetrachloride is effected as follows. Considerable amounts of phosphoric oxide are suspended in carbon tetrachloride, the suspension is cooled to 0° and violently stirred whilst perchloric acid (70%) is added drop by drop. The mixture is warmed and filtered, thus yielding a solution containing about 2·5% of chlorine heptoxide. If this solution is distilled as far as possible at 0° in a water-pump vacuum, a residue remains which contains about $\frac{1}{3}$ of the original carbon tetrachloride and 80% of the heptoxide. The vacuum is broken and the solution is digested at 70—75° and distilled in a

vacuum with a well cooled receiver up to 80°. If the product is warmed at 80°, a small distillate is obtained which contains the whole of the chlorine and chlorine peroxide, a colourless residue remaining in the flask. If more highly concentrated solutions are necessary, the residue is mixed with more phosphoric anhydride and perchloric acid and the process is repeated; thus, three successive treatments yield a solution containing 20—25% Cl_2O_7. H. W.

The Quadrupolar Moments of the Oxygen and Nitrogen Molecules. W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 939—942).—The following magnitudes were calculated: the inversion temperature of the Joule-Kelvin effect for small densities for oxygen 450°, for nitrogen 331°; the potential energy of the molecules in contact, for oxygen $5·71 \times 10^{-14}$, for nitrogen $4·77 \times 10^{-14}$; the molecular diameter for oxygen $2·65 \times 10^{-8}$, for nitrogen $2·98 \times 10^{-8}$; the quadrupolar moment for oxygen $3·55 \times 10^{-26}$ e.s.u. $\times$ cm.^{2}, for nitrogen $3·86 \times 10^{-26}$. If oxygen possesses 14 magnetons per molecule, as assumed by Weiss and Piccard the moment would be $2·6 \times 10^{-20}$; the value $9·47 \times 10^{-19}$ is required to explain the molecular attraction, hence it is concluded that the contribution of the magnetic moment to the molecular attraction does not come into consideration. J. R. P.

Non-biological Oxidation of Elementary Sulphur in Quartz Media. W. H. MACINTIRE, F. J. GRAY, and W. M. SHAW (*J. Ind. Eng. Chem.*, 1921, **13**, 310—313; *Soil Sci.*, 1921, **11**, 249—259. Compare A., 1917, i, 723).—The results of the authors' experiments show that, although the transformation of sulphur added to the soil may be partly a function of the biological content of the soil, yet sulphur may be readily and extensively converted into sulphates by independent chemical action under aerobic or anaerobic, sterile or non-sterile conditions of moist contact at normal temperatures when ferric oxides and alkaline-earth carbonates are present. T. H. P.

Vapour Pressures of Hydrogen Sulphide. E. CARDOSO (*Gazzetta*, 1921, **51**, i, 153—164).—The author has prepared highly pure hydrogen sulphide and has measured its vapour pressure at a number of temperatures between 0° and 100·4°, which is the critical point. Expression of the results by means of Biot's formula, $\log p = a + b\alpha^t + c\beta^t$, necessitates tedious calculation, and the use of logarithms of α and β containing seven significant figures if its results are to be exact to 0·05 atmosphere. The author uses, therefore, two formulæ of the type $p = ae^{bt + ct^2}$: (1) For temperatures between 0° and 50°, $\log p = 1·00860 + 0·011935t - 0·000026863t^2$ and (2) for temperatures between 50° and 100·4°, $\log p = 1·53820 + 0·0088786(t - 50) - 0·000014429(t - 50)^2$, p being expressed in atmospheres. The two parabolæ corresponding with these exponential formulæ join perfectly at 50° and permit of extrapolation over $\pm$ 6°. The two formulæ admit of the immediate deduction of the following expressions for the first differential coefficient: (1) $dp/dt = p(0·027481 - 0·00012371t)$ and (2) $dp/dt = p[0·020444 - 0·000066449(t - 50)]$. T. H. P.

The Cathodic Reduction of Dissolved Elementary Nitrogen. ERICH TIEDE and ARTHUR SCHLEEDE (*Zeitsch. Elektrochem.*, 1921, **27**, 112—114).—In 1807, Davy (*Phil. Trans.*, 1807, 1) claimed to have obtained nitric acid and ammonia by the electrolysis of distilled water containing dissolved air, but Lord Rayleigh (T., 1897, **71**, 181) failed to confirm this result. The authors have repeated the experiment under widely varying conditions, at pressures from atmospheric up to 150 atm., and have failed to obtain a trace of ammonia. E. H. R.

The Structures and Reactions of Hydroxylamine and its Derivatives. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1921, **43**, 315—332. Compare A., 1920, i, 536).—A critical review of previous work and theories on this subject, with special reference to the work of Jones (A., 1914, ii, 559). The author is of the opinion that all the properties of hydroxylamine, its derivatives, and its salts conform with and can only be satisfactorily explained by the hydroxyl structure. There is as yet no indication of the existence of such products in tautomeric forms, which, for energy and affinity reasons, under ordinary conditions, should represent labile substances. No theoretical or experimental evidence is known pointing to the existence of hydroxylamine, its derivatives, salts, or hydroxylammonium products in "electromeric" modifications and the "electronic" explanations (Jones, *loc. cit.*) of the reactions of these compounds are not tenable. W. G.

Vapour Pressure of White Phosphorus from 44° to 150°. DUNCAN MACRAE and C. C. VAN VOORHIS (*J. Amer. Chem. Soc.*, 1921, **43**, 547—553).—The vapour pressure of white phosphorus, purified with the greatest care, was measured between 44° and 150°, using the static isoteniscope described by Smith and Menzies (A., 1910, ii, 1036). From the results obtained the equation $\log P = 7{\cdot}9542 - 2757{\cdot}5/T$ is derived, P being the pressure in mm. of mercury. The maximum error is as low as 0·5% from 100° to 150°, probably increasing at lower temperatures but not exceeding 5% at 44°. The values of the vapour pressure found are from 30—60% higher than those obtained by extrapolating the equation of Smits and Bokhorst, derived from measurements between 169° and 409° (A., 1916, ii, 317). They are not inconsistent, however, with the measurements of Centnerszwer on solid white phosphorus (A., 1913, ii, 1052). E. H. R.

Preparation of Boron by the Dissociation of Boron Bromide. FRIEDRICH MEYER and R. ZAPPNER (*Ber.*, 1921, **54**, [*B*], 550—560).—Pure boron has been prepared recently by Weintraub (A., 1912, ii, 43) by the reduction of boron trichloride by hydrogen in a high-tension arc, but the process is somewhat cumbersome and not generally available. A more convenient method consists in taking advantage of the dissociability of boron bromide in the high-tension arc.

The preparation of boron bromide, b. p. 90·5°, by the action of bromine vapour on crude boron (obtained from magnesium and

boric anhydride) at 700° is described. The earlier attempts to prepare boron from it were made by striking a high-tension arc between copper poles beneath the liquid, but the yields were unsatisfactory. Subsequently, the conditions were modified, and the arc was made in the gaseous substance. For this purpose two types of apparatus are described. For the preparation of small quantities of boron, the bromide is boiled in a small bulb directly attached to a large bulb, which holds the electrodes, and thence to a reflux condenser, the whole apparatus being made of glass with ground-in joints of such a type that a little of the boron bromide condenses on them, and so shields the remainder of the product from the lubricating material; with a tension of 100,000 volts, equilibrium is established in about five hours. If larger quantities are required, a more complex apparatus is used in which the boron bromide is vaporised in a flask, from which it passes over copper wool heated at 200° (to remove free bromine), thence through the vessel containing the electrodes, then to the condenser, from which the unattacked bromide is returned to the flask.

Boron obtained by this method is an exceedingly fine, deep black powder which gradually becomes oxidised on exposure to air, reacts violently with dilute nitric acid, and inflames on contact with the concentrated acid. H. W.

The Preparation of Considerable Quantities of Pure Boron Nitride. FRIEDRICH MEYER and R. ZAPPNER (*Ber.*, 1921, **54**, [*B*], 560—566).—The preparation is beset with considerable difficulties, since all processes which utilise boric anhydride as initial material give more or less poor yields of products which are contaminated with boric acid. The only suitable starting point is the additive compound of boron trichloride and ammonia which, when led through an intensely heated tube, yields boron nitride and ammonium chloride. The operations are greatly hampered by the fact that the compound, when prepared as usual at low temperatures, is an exceedingly voluminous substance, which requires inconveniently large apparatus when used on any considerable scale and further is very hygroscopic. In addition, a large portion of the boron nitride escapes with the ammonium chloride vapour and other products from which it cannot be separated readily. This is found to be due to the fact that, as the compound approaches the hot walls of the tube, it decomposes with the evolution of sufficient gas to prevent the nitride being deposited on the tube. This difficulty is overcome by adopting a zonal arrangement of heating the reaction tube, whilst the hygroscopicity is avoided and a compact product is secured by allowing the boron chloride and ammonia to react *in situ* at an elevated temperature. The apparatus consists of a quartz tube wound with nichrome wire in three zones; it is fitted with an arrangement for the admission of hydrogen, hydrogen charged with boron chloride vapour, and ammonia, and is provided with a platinum pyrometer. The other end of the tube is fitted to a glass vessel which serves for the collection of the ammonium chloride; this vessel can be heated electrically in such a manner that a uniform deposit of the salt is

secured, thus avoiding the easy choking of the tubes. After the whole apparatus has been dried in a current of hydrogen at 300°, the tube is heated at 500—600° and regulated streams of ammonia and hydrogen charged with boron chloride are admitted, the former always being in large excess. After complete admission of the reagents, the tube is further heated in alternate zones for five to six hours, after which the temperature is gradually raised to 1000° whilst a slower current of ammonia passes over the product.

As thus prepared (the yield is 80—85% calculated on the amount of boron chloride used), boron nitride is a colourless powder the density and stability towards water of which depend on the final temperature employed; at 800° and with a long period of experiment, a very voluminous product is obtained which after exposure to the atmosphere for some time emits the odour of ammonia. More intensely heated preparations are more stable to air.

H. W.

Force of Cohesion of the Diamond. HANS THIRRING (*Zeitsch. Physik*, 1921, **4**, 1—25).—A theoretical paper in which two hypotheses are put forward as to the position of the valency electrons of carbon in the diamond. (i) The electrons circulate in paths which lie in the middle between two neighbouring nuclei. (ii) All the electrons belonging to an individual nucleus lie inside a sphere, which surrounds the atomic nucleus, the radius of which is small in comparison with the crystal lattice constant. It is shown that the first hypothesis is only usable if the cohesion is explained by the electrostatic forces, and in this connexion the general nature of homo-polar compounds is discussed. J. F. S.

Silicon Hydrides. IX. Reactions with Alkali Metals. ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1921, **54**, [*B*], 524—531).—The experiments were undertaken with the object of synthesising disilane by the action of alkali metals on monochlorosilane, but did not lead to the desired result.

Monochlorosilane reacts readily with potassium at the ordinary temperature, but the metal becomes coated with a protective layer which speedily inhibits reaction; at 300°, the change is complete, the products being silicon, potassium hydride, potassium chloride, and hydrogen. Further experiments were therefore performed with potassium–sodium alloys and with sodium amalgam, which are liquid at the atmospheric temperature; (the necessary apparatus and manipulation are fully described and illustrated in the original). With potassium–sodium alloy during a month, monochlorosilane gave only an incomplete reaction. The expected main product, disilane, could not be detected with certainty, and could have been present only in traces; the chief volatile product was monosilane, its volume being more than 60% of that of the chloro-compound used. Similar results were obtained with sodium amalgam; the chief products were monosilane mixed with a minor amount of hydrogen, but, in addition, the presence of disilane in small quantity was definitely established. The latter was shown to undergo slow decomposition in the presence of sodium–potassium alloy or of

sodium amalgam, with the production of hydrogen and monosilane. It is, however, obvious that disilane in the nascent state, probably as SiH_3, reacts far more readily with alkali metals than in the molecular form.

Methyl chloride behaves similarly to monochlorosilane towards sodium amalgam, giving methane (55%) and ethane (10%); the latter, however, is not noticeably attacked by alkali metals.

Dichloromonosilane is converted into monosilane and hydrogen by sodium amalgam.

The formation of silane and methane from their chloro-derivatives is not explained. The production of silane from disilane and sodium depends on the replacement of an atom of hydrogen by sodium and the subsequent reduction of a portion of the disilane by the nascent atom, whilst the remainder becomes condensed to non-volatile compounds. This hypothesis is supported by the observations that disilane is quantitatively reduced to monosilane by boron hydride, B_4H_{10}, which slowly decomposes at the ordinary temperature with liberation of hydrogen, and that the latter invariably accompanies monosilane in the experiments just described.

H. W.

Equilibria of Hydrofluosilicic Acid. LAWSON JOHN HUDLESTON and HENRY BASSETT (T., 1921, **119**, 403—416).

Silicic Acid. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1921, **43**, 391—396).—Experiments were made on the hydration of silica with the view of obtaining further information on the chemical relations between silica and water. Silica in the form of sand containing more than 99·0% SiO_2 was ground until 85% of the particles had a diameter less than 0·004 mm. When left in contact with water for two or three weeks, this material went into solution to the extent of about 0·032 gram per litre. The solution was truly colloidal, exhibiting the Tyndall effect, whilst the particles showed a rapid Brownian movement. When heated under pressure in presence of excess of water at 300° to 450°, the same finely-divided silica formed a gel containing 15% to 18% of water. On the other hand, silica gels prepared by dialysis of a sodium silicate–hydrochloric acid mixture under similar treatment lost water, yielding a product still containing, however, 70% to 80% of water. The hydration of fused quartz or quartz crystals can be brought about in a similar way. The action of water on silica is therefore that of a solvent, producing a silica gel, and causing it to go into the colloidal form. The more finely divided the silica, the more rapid is the action. Attempts to obtain a definite hydrate of silica, or silicic acid, by subjecting silica gels to enormous pressures, were unsuccessful, and it is concluded that the silicic acids are purely hypothetical.

E. H. R.

Synthetic Helium and Neon. A. LO SURDO (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 85—88).—The author finds that neon, helium, and hydrogen are able to pass through hot glass, the hydrogen in far greater quantity than the other two gases. The

passage is dependent on the temperature, nature, and thickness of the glass. These results may furnish an explanation for the origin of so-called synthetic helium and neon, which may be derived from the atmosphere. T. H. P.

The Electromotive Behaviour of some Binary Alloys. XV. Alloys of Potassium with Lead, Tin, and Thallium, and of Sodium with Antimony. R. KREMANN and ERNST PRESZFREUND (*Zeitsch. Metallkunde*, 1921, **13**, 19—29).—Alloys of potassium and lead containing up to 33 atoms % of lead show the same *E.M.F.*, measured against a lead electrode, as pure potassium. When the formation of the compound K_2Pb is complete, there is a sudden drop of potential to a value which again remains constant up to a composition corresponding with KPb_4. The compound KPb_2, if it exists, must have practically the same potential as K_2Pb. The potassium–tin alloys were measured against a tin electrode, and the *E.M.F.* curve indicated the formation of the compounds K_2Sn, KSn, KSn_2, and KSn_4. In the case of potassium–thallium alloys, there is a marked tendency for surface layers of the less electropositive constituent to form, so that, in alloys of even the lowest thallium content, there is a marked drop from the potassium potential. Exact determinations of the potential of the compounds KTl and K_2Tl were therefore impossible. The *E.M.F.* curve for the sodium–antimony alloys shows only one step corresponding with Na_3Sb. The potential of this compound could not be distinguished from that of NaSb. E. H. R.

A New Crystalline Form of Potassium Chlorate. E. R. WOLCOTT (*J. Ind. Eng. Chem.*, 1921, **13**, 215—216).—Potassium chlorate may be obtained in the form of long, fibrous crystals of silky appearance by treating its aqueous solution with an aqueous solution of hydrocarbons. Equal parts of California crude oil (D 0·9359) and oleum are mixed and agitated for one hour, the temperature not being allowed to rise during the operation. After some hours, the tar-like substance formed is separated from the residual acid, and dissolved in hot water to give a 6 per cent. solution. Ten c.c. of this solution are then added to 200 grams of a saturated solution of potassium chlorate, the mixture is diluted to 800 c.c., boiled, filtered, and crystallised. Preliminary friction tests in a mortar seemed to indicate less sensitiveness with these crystals than with the normal form, but this result was not confirmed with the frictional pendulum. W. J. W.

Determination of Melting Points, Especially of Potassium Chlorate. C. D. CARPENTER (*Chem. and Met. Eng.*, 1921, **24**, 569—571).—A melting-point apparatus consists of a lagged beaker, with observation holes in the lagging, a platinum resistance thermometer, and a stirrer which can be rotated at various speeds. It is heated by a molten mixture of potassium and sodium nitrate (m. p. 220°), and for temperatures above 600° both the heating bath and melting-point tube should be of transparent quartz. In determining the melting point of potassium chlorate, the sub-

stance was melted and cooled several times, the range of temperature being kept within narrow limits, and crystals never being allowed to disappear completely. The temperatures at which new crystals formed on cooling were noted in terms of the resistance. The results plotted graphically gave a resistance of 116·425 ohms, corresponding with a melting point of 357·10°. W. J. W.

Preparation of Potassium Perchlorate. E. BLAU and R. WEINGAND (*Zeitsch. Elektrochem.*, 1921, **27**, 1—10).—The thermal and electrolytic preparation of potassium perchlorate from potassium chlorate has been examined. It is shown that by heating chemically pure potassium chlorate in glass flasks to 510° a good yield of the perchlorate may be obtained. In the presence of small quantities of potassium hydroxide, copper, nickel, iron oxide, or boron trioxide, the perchlorate commences to decompose whilst there is still much undecomposed chlorate present. When commercial chlorate is used, similar results are obtained. The reaction is most efficiently carried out in quartz flasks at 480° without a catalyst; after heating for eight hours, 69 grams of perchlorate are obtained from 100 grams of chlorate. It has been found impossible to decompose completely the chlorate, for the perchlorate commences to decompose to a marked extent when there is still 3—4% of the original chlorate present. This chlorate is readily removed by crystallisation. Iron utensils are quite unsuitable for this reaction.

Potassium perchlorate can be formed by the electrolysis of a solution of potassium chlorate between a platinum anode and a nickel cathode, using a current density of 0·15 ampère/sq. dcm. A good current and material yield are obtained in the process. The process suffers from the defect that the electrodes, even with a rapidly circulating electrolyte, become incrusted with the perchlorate. With a current density of 0·1 ampère/sq. dcm. the current yield decreases if the temperature is raised above 20°, whilst with a greater current density even at 27° good yields are obtained. At 27°, the current yield increases greatly in increasing the cathodic current density, whilst a change in the anodic current density has practically no effect on the yield. If, instead of potassium chlorate, sodium chlorate is electrolysed, the very soluble sodium perchlorate is formed and this by double decomposition can be converted into potassium perchlorate by treatment with potassium chlorate. The mother liquors containing sodium chlorate are then electrolysed. In this way the incrustation of the electrodes is avoided. The electrolysis of solutions of barium chloride at 60° with a nickel cathode and a platinum anode, using a current density of 0·15 ampère/sq. dcm. gives barium perchlorate with a current yield of 50—60%. In this process the whole of the barium chloride is oxidised. The addition of acetic acid, hydrochloric acid, or calcium chloride or leading carbon dioxide into the solution are favourable to the reaction. J. F. S.

The Preparation of Sodium Hydroxide from Sodium Sulphate. BERNHARD NEUMANN and ERNST KARWAT (*Zeitsch. Elektrochem.*, 1921, **27**, 114—124).—The effects of temperature and

dilution on the equilibrium of the reaction $Na_2SO_4 + Ca(OH)_2 \rightleftharpoons CaSO_4 + 2NaOH$ were studied with the object of determining the maximum yield of sodium hydroxide which could be obtained by the action of lime on aqueous sodium sulphate. The results of earlier workers were not trustworthy because true equilibrium had not been obtained; it was found necessary to apply continuous shaking for several days. From the solubilities and dissociation constants of the reacting substances, the equilibrium constant was calculated to be $K_{18} = 0{\cdot}388$, diminishing with rising temperature. The values actually found were of this order, but considerably lower, diminishing with increasing temperature or increasing concentration. The results of the experiments at 15°, 40°, 70°, and 100° are shown in a series of curves in which the "yield" of sodium hydroxide is plotted against the dilution of sodium sulphate taken. On each curve the yield is highest at the greatest dilution and at any dilution it is highest at the lowest temperature [compare *J. Soc. Chem. Ind.*, 1921, 257A]. E. H. R.

Preparation and Properties of Sodamide. J. M. McGee (*J. Amer. Chem. Soc.*, 1921, **43**, 586—591).—Sodamide melts sharply at 208° (compare Titherley, T., 1894, **65**, 504), and at 210° has a specific conductivity of $1{\cdot}665 \pm 0{\cdot}005$ mhos, using platinum electrodes (compare Wöhler and Stang-Lund, A., 1918, ii, 397). Values were not obtained above this temperature owing to catalytic decomposition of the amide by platinum into ammonia and either sodium imide or nitride. No blue solutions of sodium in the amide could be obtained (compare Titherley), and the solvent action on glass imputed to the amide by Titherley and others was probably due to sodium hydroxide, since no tendency of this kind was observed below 240°. At 270—300°, however, there was a slight action after two to three days. J. K.

Melting Point of Ammonium Sulphate. James Kendall and Arthur W. Davidson (*J. Ind. Eng. Chem.*, 1921, **13**, 303—304).—Widely divergent values have been given for the melting points of ammonium sulphate and ammonium hydrogen sulphate. For the latter salt, Kendall and Landon (this vol., ii, 45) found m. p. $146{\cdot}9 \pm 0{\cdot}5°$, Jänecke's value, 251° (A., 1920, ii, 757), being grossly inaccurate. The normal sulphate loses ammonia, even at 200°, so that determination of a true melting point in an open tube is impossible. When the salt is heated gradually in a sealed tube which it practically fills, it softens perceptibly at 490° and gives m. p. $513 \pm 2°$; this temperature represents, then, the definite melting point of normal ammonium sulphate under an ammonia pressure of considerably more than 1 atmosphere. Caspar's value, 417—423° (A., 1920, ii, 431), is thus erroneous, as also is Jänecke's statement (*loc. cit.*) that the normal sulphate has the same m. p. and b. p., 357°. T. H. P.

Colloidal Calcium Phosphate. G. M. de Toni (*Kolloid Zeitsch.*, 1921, **28**, 145—148).—Colloidal calcium phosphate may be prepared by adding, slowly and with continuous shaking, a hot

normal solution of sodium phosphate to an equal volume of a hot normal solution of calcium chloride containing a definite amount of a protective colloid. The colloidal solution is best obtained in the presence of gelatin, but may also be prepared in the presence of gum arabic, blood serum, and starch; in the presence of sucrose and caramel, the colloid is not produced. The amount of protective colloid controls the concentration of colloidal calcium phosphate present in the solution; thus with 9·5 grams of gelatin per litre the colloidal solution contains 2·068 grams of calcium phosphate, and with 27·5 grams of gelatin, 4·137 grams of calcium phosphate. The colloidal solution is practically opaque and is quite clear in transmitted light, but bluish-white in colour by reflected light. The gel is porcelain-white, with a faint blue tinge by reflected light. The individual particles are invisible under a magnification of 1800. The colloidal solution may also be obtained by the action of a solution of orthophosphoric acid on a solution of calcium hydroxide containing gelatin. The importance of colloidal calcium phosphate in therapeutics and its possible rôle in the processes of assimilation and digestion are indicated. J. F. S.

Transformation of Light Magnesia into the Dense Form. N. PARRAVANO and C. MAZZETTI (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 63—66).—The results of the authors' experiments show that the velocity of hydration of magnesium oxide diminishes as the temperature and duration of its previous calcination are increased, no discontinuity being observable. The statement that magnesium oxide undergoes transformation at about 1600° (Le Chatelier, *Le Chauffage*, 399) or 1100° (Campbell, A., 1918, ii, 364) is inaccurate, this change having already begun at the lowest temperature employed by the authors, namely, 800°, at which, however, it proceeds very slowly. This result is confirmed by Ditte's measurements of the density of the oxide after being heated at definite temperatures for a certain time (this Journ., 1871, 869). Natural magnesites contain impurities which exert a marked influence on the velocity of hydration of the oxide resulting from their calcination, the transformation into the dense modification being facilitated. This change is at first slow and continually increases in rapidity as the temperature is raised, and no definite transformation temperature probably exists. T. H. P.

Constitution of Alloys of Aluminium, Copper, and Zinc containing High Percentages of Zinc. JOHN L. HAUGHTON and KATHLEEN E. BINGHAM (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 47—69).—The thermal curves, microscopic appearance of annealed and quenched specimens, and the electrical conductivities were determined and the results represented by diagrams. J. R. P.

The so-called Oligodynamic Action of the Heavy Metals and of the Salts of the Heavy Metals. W. FALTA and M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1921, **115**, 39—41).—The oligodynamic action of various metals was tested in the following way: a test-tube was filled with water containing the respective metals and left for eight days. The metal and the water were

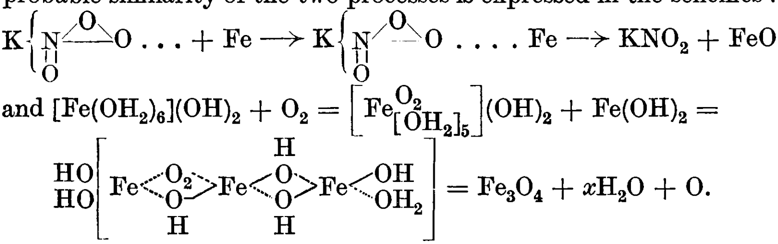
then removed, the test-tube rinsed out with distilled water, and its oligodynamic action tested on the different solutions. It was found that guaiacol, benzidine, resorcinol, and homogentisic acid were oxidised when kept in test-tubes prepared in the above way. Potassium permanganate was decolorised, with the formation of manganese dioxide. Methylene-blue, indigotin, and sodium indigotinsulphonate were decolorised and the leuco-base of malachite-green was oxidised. Protein solutions were coagulated through the oligodynamic action of the metals. The hydrolysis of starch was, however, not brought about in this way. This oligodynamic action was shown by the following metals, which are arranged in the order of their activity: copper, mercury, silver, lead, tin, aluminium, iron, magnesium, and platinum. S. S. Z.

The Reaction between Copper and Nitrogen Peroxide. HERMAN V. TARTAR and WALDO L. SEMON (*J. Amer. Chem. Soc.*, 1921, **43**, 494—500).—By the action of dry nitrogen peroxide on copper powder prepared by the reduction of cupric oxide in a stream of hydrogen or carbon monoxide, Sabatier and Senderens (A., 1893, ii, 374) obtained a product to which they ascribed the formula Cu_2NO_2. The authors have repeated this work, using powdered copper prepared (*a*) by the reduction of cupric oxide with hydrogen and (*b*) by the reduction of hydrated cuprous oxide, $4Cu_2O,H_2O$, with carbon monoxide. The hydrated cuprous oxide was prepared by precipitating a hydrochloric acid solution of cuprous chloride with sodium hydroxide solution, and the composition of the product so obtained confirmed the formula given by Mitscherlich to this substance. The copper reduced by hydrogen reacted immediately and at a fairly rapid rate with nitrogen peroxide, whilst that reduced by carbon monoxide only darkened after several hours, and took several days before the reaction was complete. The final gain in weight was variable in different experiments and the final product was a mixture containing much unchanged copper. The ratio of nitrogen to oxygen in the product immediately after withdrawing it from the gas was 1 : 3, but on exposure to the air loss of weight occurred, nitric oxide or nitrogen peroxide being evolved. The formula Cu_2NO_2 cannot be confirmed, and it is suggested that anhydrous cuprous nitrate is formed on the surface of the copper. At the same time, doubt is thrown on the existence of other compounds said to have been obtained by the action of nitrogen peroxide on metals. E. H. R.

The Action of Additions on the Anomaly of Dilatation of Ferronickels; Application to Iron–Nickel–Chromium Alloys. P. CHEVENARD (*Compt. rend.*, 1921, **172**, 594—596).—By plotting the total anomaly of dilatation, A_0, against the composition of pure ferronickels, a curve is obtained which rises rapidly with the nickel content from 25% nickel, reaches a sharp maximum at a point corresponding with the compound Fe_2Ni, and then descends rapidly to reach a value $A_0 = 0$ at about 58% nickel, when A_0 becomes negative. The curve recrosses the zero line again at 80% and 99% nickel. On the addition of chromium to such alloys, similar curves

are obtained, but the maximum is less in value and is displaced towards a higher nickel content. W. G.

The Peculiar Chemical and Physical Properties of Ferrous Hydroxide Peroxide. Reduction of Alkali Nitrate. OSKAR BAUDISCH (*Ber.*, 1921, **54**, [*B*], 406—413). It has been shown previously that ferrous hydroxide in neutral or faintly alkaline solution is unable to effect the reduction of nitrate to nitrite and that this well known process is attributable to the co-operation of atmospheric oxygen. It is now demonstrated that nascent ferrous hydroxide is a much more powerful reducing agent towards nitrate than the freshly precipitated compound, and, further, that nitrate is smoothly converted into nitrite by reduced iron in the absence of air. The probable similarity of the two processes is expressed in the schemes:



The ferrous hydroxide can thus yield an energetic peroxide by absorption of oxygen, which, by virtue of its iron nucleus, possesses the power of activating the oxygen subsidiary valencies of other substances and forming unstable compounds with them.

Ferrous hydroxide peroxide can also function as an oxidising agent, as is shown by the conversion of alcohol to aldehyde and by its behaviour towards starch and sugar. It acts in this respect in the same manner as light energy alone or in the presence of traces of iron. Since also it can effect the reduction of alkali nitrate to ammonia, it appeared probable that both types of reaction could occur in one and the same solution; this is shown to be the case, since formaldoxime and traces of nitromethane are formed when a methyl alcoholic, aqueous nitrite solution is treated with ferrous sulphate and an excess of sodium hydrogen carbonate and shaken with air. The nitrite is reduced to hyponitrous acid, which reacts with the formaldehyde produced by the oxidation of methyl alcohol, yielding formhydroxamic acid, which is in part converted into formaldoxime.

It is remarkable that metallic iron and ferrous hydroxide peroxide are strongly magnetic, whereas ferrous hydroxide is not; it does not appear possible at present to bring these properties into line with the chemical behaviour. H. W.

Anhydrous Yellow Ferric Oxide. JOHN H. YOE (*J. Physical Chem.*, 1921, **25**, 196—200).—Anhydrous yellow ferric oxide was obtained in admixture with aluminium oxide, calcium sulphate, barium sulphate, aluminium oxide, and calcium sulphate, and aluminium oxide and barium sulphate. The results confirm and extend the observations of Scheetz (A., 1917, ii, 574). Attempts to

remove the stabilising agent, for example, by dissolving aluminium oxide in sodium hydroxide, invariably resulted in agglomeration of the ferric oxide, with change of colour to red. J. R. P.

Double Pyrophosphate of Iron and Sodium. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, **51**, i, 130—137).—This compound, which has the composition, $Fe_4(P_2O_7)_3,3Na_4P_2O_7,14H_2O$, and not $Fe_4(P_2O_7)_3,5Na_4P_2O_7,14H_2O$, as stated by Pahl (This Journal, 1874, 338, 774), may be prepared pure by saturating sodium pyrophosphate solution with moist ferric pyrophosphate with the aid of a mechanical stirrer, the dissolution of the calculated amount of sodium pyrophosphate in ferric chloride solution of D 1·28—1·282, followed by precipitation of the double salt by means of alcohol, giving a product containing sodium chloride; in presence of the latter, the solubility of the double pyrophosphate is lowered. Ferric pyrophosphate dissolves in sodium pyrophosphate solution always in the proportion $Fe_4(P_2O_7)_3 : 3Na_4P_2O_7$, independently of the concentrations. Ferric phosphate is soluble also in alkaline citrate solutions, yielding complex salts in which the reactions for iron are masked. T. H. P.

A Comparison of the Atomic Weights of Terrestrial and Meteoric Nickel. I. The Reduction of Nickelous Oxide. GREGORY PAUL BAXTER and LEON WOODMAN PARSONS (*J. Amer. Chem. Soc.*, 1921, **43**, 507—518).—To compare the atomic weights of terrestrial and meteoric nickel, the method by the reduction of nickelous oxide with hydrogen was chosen, as it would also serve to check the atomic weight determination made by Richards and Cushman (A., 1898, ii, 228) by analysis of the bromide. The nickelous oxide was in each case prepared by ignition of the nitrate, and since it is impossible to free the oxide from occluded gases at the temperature used, 1000°, it was necessary to make independent determinations of the occluded gases in each sample. The oxide generally contained about 0·11% of gases. As a result of nine determinations with terrestrial material, a mean atomic weight of 58·70 was found, whilst three experiments with meteoric nickel gave 58·68. The value found by Richards and Cushman was 58·68 (Ag = 107·88). The difference found between terrestrial and meteoric nickel is considered to be within the limits of experimental error, but further comparisons are to be made. E. H. R.

Solubility. II. Polyiodides of Ammines. FRITZ EPHRAIM and PAUL MOSIMANN (*Ber.*, 1921, **54**, [*B*], 385—396).—An account of experiments on which a part of the authors' theory (this vol., ii, 305) is based.

Nickelhexammine chloride or a solution of nickel chloride in ammonia, is transformed by relatively varying quantities of iodine dissolved in potassium iodide into a series of polyiodides of which members, corresponding approximately with the formulæ $[Ni(NH_3)_4]I_2,I_2$, $[Ni(NH_3)_4]I_2,2I_2$, $[Ni(NH_3)_4]I_2,4I_2$, and $[Ni(NH_3)_4]I_2,6I_2$ have been isolated. It does not appear probable, however, that these are well-defined individuals of a series of compounds, but rather that a continuous series of solid solutions is produced. A solution of zinc sulphate in concentrated ammonia is

only converted by a large excess of iodine into *zinctetrammine polyiodide*, $[Zn(NH_3)_4]I_2,2I_2$, dark violet leaflets. Similarly, cadmium sulphate gives the *compound* $[Cd(NH_3)_3H_2O]I_2,2I_2$. With a large excess of iodine, *coppertetrammine polyiodide*, $[Cu(NH_3)_4]I_2,4I_2$, is obtained as a blackish-brown, not distinctly crystalline precipitate; with smaller amounts of the halogen, polyiodides with a lower iodine content which have been described previously are produced. Cobalt appears to form a *polyiodide*, $[Co(NH_3)_4]I_2,2I_2$, but its isolation in a pure condition is extremely difficult by reason of the great oxidisability of ammoniacal cobalt solutions. Magnesium and calcium salts yield nitrogen iodide when treated with potassium polyiodide in ammoniacal solution, even in the presence of ammonium salts.

Cobalthexammine chloride gives a *polyiodide*, $[Co(NH_3)_6]I_3,2I_2$, bluish-black crystals, and, with a very large excess of iodine, a *compound*, $[Co(NH_3)_6]I_3,3I_2$, transparent, brown needles. A similar *polyiodide*, $[Cr(NH_3)_6]I_3,3I_2$ is obtainable from luteochromium compounds.

The freely soluble cis-*compound*, $[Co(NH_3)_4(NO_2)_2]I$, yellow octahedra, is prepared from the corresponding nitrate and an excess of potassium iodide in aqueous alcoholic solution; it yields two *polyiodides*, $[Co(NH_3)_4(NO_2)_2]I,I_2$, slender, green needles and $[Co(NH_3)_4(NO_2)_2]I,2I_2$, black crystals, the limit of additive capacity for iodine being probably attained in the latter compound. The similar trans-*compound*, $[Co(NH_3)_4(NO_2)_2]I$, forms yellow, distorted cubes, and yields a tri-iodide, reddish-brown precipitate, without distinct crystalline form, the relatively pale colour of which makes it doubtful if the product is a true polyiodide. *Cobalt-tetrammine-carbonatopolyiodide*, $[Co(NH_3)_4(CO_3)]I,I_2$, forms black, crystalline aggregates.

The stability of the various polyiodides has been investigated by repeated agitation of the solid substances with fixed amounts of carbon disulphide and estimation of the amount of iodine which has passed into solution after equilibrium has been established, the method being, when necessary, controlled by analysis of the residual solid. Among the penta-iodides of the ammines of bivalent metals, it is found that iodine is more firmly retained with increasing atomic volume of the metal. The nickel compounds readily lose the whole of the iodine, the compound $[Ni(NH_3)_4]I_2,I_2$ forming a well-marked intermediate stage. The cadmium compound retains iodine much more firmly, and this phenomenon is even more marked with the zinc salt. $[Co(NH_3)_4(CO_3)]I,I_2$ retains the polyiodide iodine very firmly, $[Co(NH_3)_4(NO_2)_2]I,I_2$ with medium tenacity. $[Co(NH_3)_6]I_3,3I_2$ readily parts with all its iodine. In general, the capacity to lose iodine completely is exhibited by those substances which have the power of becoming rich in iodine, but this behaviour may be merely accidental. H. W.

Solubility. III. Compounds Derived from Ammines and Bismuth or Mercury Iodides. FRITZ EPHRAIM and PAUL MOSIMANN (*Ber.*, 1921, **54**, [*B*], 396—401. Compare preceding abstract).—The following compounds were prepared by the

addition of bismuth or mercuric salts dissolved in an excess of potassium iodide solution to solutions of the requisite ammine. The bismuth compounds could be obtained only from ammines of tervalent cobalt. *Hexamminocobaltibismuth iodide*, $[Co(NH_3)_6]I_3,BiI_3$, small, dark-red, pointed crystals; *chloropentamminocobaltibismuth iodide*, $[Co(NH_3)_5Cl]I_2,2BiI_3$, red, microcrystalline powder; *dinitrotetramminocobaltibismuth iodide*, $[Co(NH_3)_4(NO_2)_2]I,BiI_3$ (flavo-salt, red, hexagonal rods, croceo-salt, microcrystalline powder); *carbonatotetramminocobaltibismuth iodide*, $[Co(NH_3)_4(CO_3)]I,BiI_3$, reddish-yellow granules. The following nickel–ammine mercury *iodides* are described: $[Ni(NH_3)_4]I_2,HgI_2,4H_2O$, $[Ni(NH_3)_6]I_2,HgI_2,8H_2O$, $[Ni(NH_3)_4]I_2,2HgI_2,2H_2O$, $[Ni(NH_3)_6]I_2,2HgI_2,8H_2O$. The first and second of these are obtained with an excess of nickel salt, the third and fourth when the mercuric salt predominates; the tetrammines are prepared in feebly, the hexammines in more strongly, ammoniacal solution. The former are greenish-blue, the latter pale violet. Zinc salts yield only the *compound*, $[Zn(NH_3)_4]HgI_4$, colourless or pale yellow octahedra or cubes; the cadmium *compounds*, $[Cd(NH_3)_4]HgI_4,4H_2O$ and $[Cd(NH_3)_6]HgI_4,6H_2O$, are formed in less or more strongly ammoniacal solution respectively. Under similar conditions, a very unstable silver salt appears to be formed. Cobalt gives only a very basic compound, whilst magnesism and manganese salts do not give precipitates with potassium mercuric iodide.

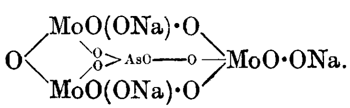
Carbonatotetramminocobaltimercury iodide,

$$\{[Co(NH_3)_4(CO_3)]I\}_2,HgI_2,$$

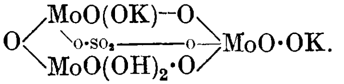
crystallises in red rhombs. The flavo-salt of *dinitrotetramminocobaltimercury iodide*, $[Co(NH_3)_4(NO_2)_2]I_2,HgI_2$, forms brown needles, whereas the *croceo*-salt crystallises in yellow octahedra. *Hexamminocobaltimercury iodide*, $[Co(NH_3)_6]I_3,HgI_2$ is a reddish-brown, shining powder.

Hexamminocobaltiferrocyanide, $[Co(NH_3)_6]_4[Fe(CN)_6]_3$, is prepared from potassium ferrocyanide and luteocobalt chloride; with the purpureo-chloride, the two dinitrotetramminocobalti- and the carbonatotetramminocobalti-compounds, potassium ferrocyanide gives colloidally turbid solutions which gradually deposit precipitates owing to decomposition. Potassium ferricyanide does not give precipitates with the cobaltammines mentioned above with the exception of the luteo-salt. H. W.

System and Constitution of Complex Derivatives of the Molybdic Acids. L. Forsén (*Compt. rend.*, 1921, **172**, 681—684. Compare this vol., ii, 205).—The complex acids may be grouped in three general series, namely, (1) complex orthomolybdic acids of the type $H_3(AsOMo_3O_{12})$, (2) complex metamolybdic acids of the type $H_3(AsOMo_{12}O_{42}H_6)$ or $H_4(SiOMo_{12}O_{42}H_6)$, (3) complex luteomolybdic acids of the type $AsO(Mo_3O_{12}H_5)H_3$. Arsenio-*o*-molybdic acid is tribasic and its sodium salt is assigned the annexed constitution. Phospho-*o*-molybdic acid is not known, but some of its salts are. Sulphato-*o*-molybdic acid



is not known, but the author has prepared a new *potassium* salt, $K_2H_2(SO_2Mo_3O_{12}),3H_2O$, which rapidly loses $4H_2O$ and on heating gives anhydrous potassium trimolybdate. It probably has the annexed constitution. Too few salts of the complex metamolybdic acids are known for their constitution to be discussed. The free luteo-acids are very stable and tribasic, and to them is assigned the constitution of the type



$$AsO\left[O{\cdot}MoO(ONa){<}{}^{O\cdot MoO(OH)_2}_{O\cdot MoO(OH)_2}{>}O\right]H_3.$$ W. G.

A System for the Molybdates. S. Posternak (*Compt. rend.*, 1921, **172**, 597—599).—The author does not consider that the system recently proposed by Forsén (this vol., ii, 205, 265) complies with the experimental facts which he has published (A., 1920, ii, 374; this vol., ii, 51, 117, 118). W. G.

Volume Changes of Tin Amalgams. Carola Köller (*Zeitsch. Metallkunde*, 1921, **13**, 1—19).—The volume changes of tin amalgams having the compositions HgSn, $HgSn_2$, $HgSn_3$, and $HgSn_4$ were investigated by the dilatometer method. With increasing temperature the coefficient of expansion first falls or remains practically constant over a considerable range, then rises rapidly to a maximum corresponding practically with the melting point of the amalgam. This abnormal behaviour is due to volume changes similar in character to those occurring in the case of bismuth amalgam and some other alloys. When the tin amalgam is alternately heated and cooled, the final volume is always less than the initial volume. Contraction also occurs when the freshly-prepared alloy is maintained at a steady temperature for some time, the rate of contraction depending on the previous treatment to which the specimen has been subjected. The nature of the structural changes responsible for this behaviour has not been elucidated. E. H. R.

Preparation of Zirconia from Brazilian Ore and a New Method of Estimation. E. C. Rossiter and P. H. Sanders (*J. Soc. Chem. Ind.*, 1921, **40**, 70—71T).—Fifty grams of the powdered ore are fused in an iron crucible with 50 grams of sodium hydroxide; the mixture is stirred until frothing ceases, and a granular powder is obtained, the heating being then continued at dull redness for two hours. The mass, while hot, is poured into 1·5 litres of water, the solution filtered, the insoluble residue treated with hydrochloric acid, and evaporated to dryness. The dry residue is extracted with hot water and the solution filtered. This solution is diluted to 1·5 litres, boiled after the addition of a slight excess of sulphurous acid, and $N/1$ sulphuric acid is added gradually until the mixture becomes quite thick. After a short time the whole of the zirconia is precipitated as basic sulphate; the precipitate is collected, washed, dried, and ignited to form the oxide, or the precipitate may be suspended in water, treated with alkali,

and the hydroxide collected, dried, and ignited. A modification of the process may be used for the estimation of small quantities of zirconia in the presence of iron, etc. The solution, containing about 0·2 gram of ZrO_2, is diluted to 150 c.c., boiled with the addition of sulphurous acid (to reduce ferric salts), neutralised with ammonia, and again boiled after the addition of 10 c.c. of sulphurous acid and 2 c.c. of $N/1$ sulphuric acid. The precipitated basic sulphate is collected, dissolved in hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water, and the zirconia reprecipitated as described, ignited, and weighed. W. P. S.

The Electromotive Behaviour of some Binary Alloys. XVII. Antimony–Selenium Alloys and their Metallographic Investigation. ROBERT KREMANN and ROBERT WITTEK (*Zeitsch. Metallkunde*, 1921, **13**, 90—97).—The *E.M.F.* of antimony–selenium alloys were measured against a reference electrode of antimony, using a hydrochloric acid solution of antimony trichloride as electrolyte. The experiments were conducted in darkness or in diffused daylight on account of the sensitiveness to light of the selenium alloys. The *E.M.F.*-composition curve departs considerably from the ideal stepped form, but indicates clearly the potentials of the compounds SeSb and Se_3Sb_2. This divergence from the ideal form of curve is probably due to the formation of surface layers of lower potential, causing a too early drop in *E.M.F.* The microscopic appearance of the alloys confirms the existence of the above two compounds. E. H. R.

The Electromotive Behaviour of some Binary Alloys. XVI. Alloys of Bismuth with Sodium and Potassium. ROBERT KREMANN, JULIUS FRITSCH, and RICHARD LIEBL (*Zeitsch. Metallkunde*, 1921, **13**, 66—73).—The potential of sodium–bismuth alloys was measured against a bismuth electrode in a pyridine solution of sodium iodide, or in aqueous sodium sulphate in the case of the alloys poor in sodium. Concordant results could not be obtained owing to the formation of surface layers, but in general, with from 10 to 80 atom. % of bismuth, the *E.M.F.* was constant at about 1·6 to 1·7 volts, about 0·4 to 0·5 volt below the sodium potential. For measuring the potential of potassium–bismuth alloys against bismuth, a pyridine solution of potassium chloride was used. With these alloys there was little tendency for surface layers of lower potential to form, and the *E.M.F.* curve showed two sharp steps corresponding with K_3Bi at 1·60 volts and KBi_2 at about 0·80 volt. E. H. R.

Gold Sols. ERICH VON KNAFFL-LENZ (*Kolloid Zeitsch.*, 1921, **28**, 149—153).—A number of gold sols prepared by different methods have been examined with the object of ascertaining whether the reducing agent employed influences the properties of the sol to a marked extent and also to ascertain whether gold sols are to be regarded as complexes of a gold compound with the oxidation product formed in the reduction process or no. The sols examined were prepared from a dilute aqueous solution of chloroauric acid which was reduced in the presence of potassium carbonate at the

boiling point by acetaldehyde, trichloroacetaldehyde, benzaldehyde, cinnamaldehyde, terephthalaldehyde, and arsenic hydride, respectively. The sols thus produced were examined in respect of their specific conductivity, stability, colour, and the action of hydrochloric acid, potassium chloride, barium chloride, and albumin toward them. The results show that whilst there are minor differences to be found between the behaviour of the various sols, these are such as to be attributable to slight differences in the concentration of the chloroauric acid from which the sols were made, and are entirely insufficient to furnish any confirmation of the hypothesis of complex compound formation. Tests made with the sols produced by reduction with arsenic hydride show that a very small quantity of arsenic is retained by the dialysed sol, but the amount of arsenic present divides itself between the gel and the filtrate when the sol is coagulated. The sols from terephthalaldehyde, when treated with arsenic hydride, behave in exactly the same way. J. F. S.

Mineralogical Chemistry.

Some Constituents of Lignites. R. CIUSA and A. GALIZZI (*Gazzetta*, 1921, **51**, i, 55—60).—The xyloid lignite of Fognano, near Montepulciano, contains a white, crystalline incrustation which, after purification, has the formula $C_{15}H_{20}$, m. p. 61—62°, b. p. 314—316° or 208—210°/23 mm., and constitutes a new mineral species, for which the name *simonellite* is suggested. It forms brittle, rhombic plates [G. BOERIS—$a : b : c = 0·9908 : 1 : 1·9694$], does not decolorise bromine or permanganate solution, but is oxidised by alkaline permanganate or by chromic acid, yielding a red substance with the appearance and behaviour of a quinone. Besides simonellite, the Fognano lignite yields a liquid which, on fractionation, gives three dense, colourless, odourless liquids behaving as unsaturated hydrocarbons and having the properties and compositions: (1) $C_{15}H_{28}$, b. p. 222—228/25 mm.; (2) $C_{15}H_{28}$, b. p. 240—244°/25 mm., and (3) $C_{15}H_{26}$, b. p. 253°/25 mm.

A lignite deposit near Terni contains the hydrocarbon $C_{20}H_{34}$, which forms feathery masses of crystalline plates, m. p. 74—75°, and is possibly identical with the natural hydrocarbon, hartite.

The material known commercially as Forli lignite has more the character of peat and is found to contain lignoceric acid.

T. H. P.

Minerals of Lazio. Melilite of Inclusions in Peperino. F. MILLOSEVICH (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 80—84).—The peperino used for the foundations of the Villa Volterra at Albano (Latium) was found to contain clear, bright crystals of melilite having the composition:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Total.
41·07	10·47	3·80	33·92	6·02	3·25	1·04	99·57

and the constants, D^{15} 2·929, $a : c = 1 : 0·45643$. If, as Schaller considers (A., 1916, ii, 632), melilites consist of isomorphous mixtures of sarcolite, a hypothetical soda-sarcolite, velardeñite, and åkermanite, the sample now described contains 27·5, 9·0, 15·0, and 48·5% respectively of these components. T. H. P.

Analytical Chemistry.

Spot Reactions in Qualitative Analysis. E. HAUSER (*Zeitsch. anal. Chem.*, 1921, **60**, 88—91).—The author agrees with Feigl and Stern (this vol., ii, 278) as to the usefulness of spot reactions in qualitative analysis. W. P. S.

Physico-chemical Volumetric Analysis. R. DUBRISAY (*Ann. Falsif.*, 1921, **14**, 9—18).—The advantages of physico-chemical methods of titrations are dealt with, particular attention being directed to electro-chemical, cryoscopic, and surface tension methods (compare A., 1913, ii, 586). W. P. S.

A Process of Spectrum Analysis by Means of Röntgen Rays. MANNE SIEGBAHN, AXEL E. LINDH, and NILS STENSSON (*Zeitsch. Physik*, 1921, **4**, 61—67).—A vacuum spectrograph is described by means of which the X-ray spectrum may be used for spectrum analysis of mixtures in the ordinary course of analysis. The instrument is built with a wide opening angle, about 40°, and with a fixed calcspar or gypsum crystal so that with two exposures, each approximately two hours in duration, it is possible to obtain a photograph of the lines corresponding with all the elements from sodium to uranium. This method is to be recommended because of the relative simplicity of the spectra. The identification of the lines is simplified by the use of keys prepared for each crystal used in the instrument. J. F. S.

The Importance of Adsorption in Analytical Chemistry. VIII. The Adsorption of Asbestos. I. M. KOLFTHOF (*Pharm. Weekblad*, 1921, **58**, 401—407).—Ordinary commercial asbestos, even that specially prepared for analytical purposes, cannot safely be used without having first been repeatedly extracted with acid. No adsorption will occur if the asbestos has been so treated until it no longer takes up acid from the solution.

Impure asbestos adsorbs positive ions from solutions in accordance with the adsorption law, $x=\alpha c^{1/n}$, where x is the amount adsorbed in milli-moles per gram of asbestos, c is the end concentration, and α and $1/n$ are constants. The constant $1/n$ has the same value for kations of the same valency, and appears to vary inversely with the valency for uni- and bi-valent kations. On account of the ease with which lead is adsorbed from dilute

solutions by such impure asbestos, being afterwards readily dissolved out again by means of acids, the estimation of this metal in drinking water may conveniently be carried out with asbestos.

S. I. L.

Apparatus for Sodium Peroxide Fusions. H. J. HODSMAN (*J. Soc. Chem. Ind.*, 1921, **40**, 74T.).—The mixture of sodium peroxide and substance to be oxidised is placed in a thin-walled steel cylinder which is closed at the bottom and provided with a closely-fitting cap; this cylinder is placed in an outer cylinder, the lid of which is held in place by a bayonet catch, which, when drawn up, holds the cap of the inner cylinder in place. The apparatus is clamped in an inclined position, and the base is heated with a burner until firing has occurred.

W. P. S.

Analysis of Fluorides. EDUARDO D. GARCÍA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 235—241).—A review of earlier methods is given. In Doyle's method (A., 1919, ii, 349) an error is caused by the loss of fluorine as aluminium fluoride. In the method proposed, calcium is determined in the residue from the treatment with acetic acid (as in Doyle's method) after removal of silica, iron, and aluminium. The amount of calcium fluoride is calculated on the assumption that all the calcium in the residue is present as such.

G. W. R.

Estimation of Nitrous Fumes in Air, with Special Reference to Fuse-igniters. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1921, **4**, 3—7).—A definite quantity of nitrite solution is heated at 50° with 10 c.c. of *p*-nitroaniline solution (*p*-nitroaniline 1·5 grams, concentrated hydrochloric acid 40 c.c., and water to 500 c.c.), 10 c.c. of α-naphthol solution (α-naphthol 2 grams, sodium hydroxide 1·1 grams, sodium acetate 10 grams, and water to 500 c.c.) are then added and, after one hour, the orange-red precipitate is collected and weighed; 92 parts of NO_2, or 69 parts of sodium nitrite, yield 292 parts of precipitate. To estimate NO_2 apart from nitrite in the fumes produced by fuse-igniters, the gas is left in contact with neutral hydrogen peroxide solution for twenty-four hours, and the acidity then titrated with sodium hydroxide solution, using methyl-orange as indicator; each c.c. of $N/10$-alkali solution is equivalent to 0·0060 gram of NO_2. An alternative method consists in agitating the fumes for six hours with 5% potassium iodide solution and then titrating the liberated iodine with thiosulphate solution; each c.c. of $N/10$-solution is equivalent to 0·0051 gram of NO_2. This method can be applied only in neutral solution.

W. P. S.

Comparative Results with Scales's [Zinc–Copper Couple] and Devarda's Alloy for Reducing Nitric Nitrogen. A. P. HARRISON (*J. Biol. Chem.*, 1921, **46**, 53—56).—Scales's zinc–copper couple (A., 1917, ii, 41) gives as accurate results as Devarda's alloy, and has the advantage of not requiring to be weighed. Two hundred c.c. of the solution with 0·1 mg. *N* per c.c. is poured into a flask containing 80 grams of freshly prepared zinc–copper couple,

about 5 grams of sodium chloride and 1 gram of magnesium oxide are added, and 150 c.c. distilled into a flask containing 50 c.c. of 4% boric acid. It is titrated with bromophenol-blue as indicator.

G. B.

The Diphenylamine Reaction. ALBERT B. WEINHAGEN (*J. Amer. Chem. Soc.*, 1921, **43**, 685).—The statements of Harvey (A., 1920, ii, 504) in regard to the influence of varying proportions of water are confirmed. Satisfactory results have been obtained by stirring the substance under examination with ten drops of a solution of diphenylamine in sulphuric acid by the aid of a glass rod moistened with water. Successive additions of water in this manner involve little risk of missing the most favourable concentration for the reaction.

J. K.

Iron as the Cause of a Formaldehyde and Diphenylamine Reaction of Milk. F. REISS (*Zeitsch. Nahr.-Genussm.*, 1921, **41**, 26—29).—Traces of iron in milk cause the latter to give reactions with formaldehyde and with diphenylamine–sulphuric acid reagent and thus erroneously indicate the presence of nitrates. The iron may be derived from the vessels (rusty cans) in which the milk is kept.

W. P. S.

Decomposition of Nitrous Acid. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, **51**, i, 138—140).—The action of hydrazoic acid on nitrous acid proceeds quantitatively in accordance with the equation $HNO_2 + HN_3 = H_2O + N_2O + N_2$, the unstable suboxide, N_4O, being probably formed as an intermediate product; no trace of nitric acid is formed.

This reaction may be employed for the detection of nitric acid in presence of nitrous acid, other methods for such detection yielding uncertain results owing to the formation of appreciable traces of nitric acid by partial decomposition of the nitrous acid. The test is carried out as follows: To the solution containing nitric and nitrous acids, acidified with acetic acid when the nitrous acid is present as salt, are added either a few c.c. of dilute hydrazoic acid solution or a little of its sodium salt. The liquid is then boiled to expel, as far as possible, excess of hydrazoic acid, which masks all the colour reactions employed to identify nitrates and nitrites. After the heating, a portion of the liquid is tested with an acetic acid solution of naphthylamine and sulphanilic acid to ascertain if all the nitrous acid has been destroyed, the remainder being examined for nitric acid.

T. H. P.

Estimation of Phosphorus in Copper Phosphide. EDUARDO D. GARCÍA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 104—105).—Solution is effected by means of hydrochloric acid and potassium chlorate. Group II metals are removed by means of hydrogen sulphide. The filtrate is concentrated and boiled with a little nitric acid, aluminium sulphate is added, and by addition of ammonia all the phosphorus is precipitated as aluminium phosphate. This is dissolved in nitric acid and the phosphorus estimated by the ordinary phosphomolybdate method.

G. W. R.

Estimation of Phosphorus in Steels. Separation of the Phosphorus from the other Components of the Steel. R. Ariano (*Gazzetta*, 1921, **51**, i, 1—31).—The theoretical considerations involved in the estimation of phosphorus in steel are discussed, as well as (1) the methods used for the separation of the silicon, copper, arsenic, etc., and (2) the precipitation of the phosphorus by the acetate method and by the phosphomolybdate method [see *J. Soc. Chem. Ind.*, 1921, May]. T. H. P.

The Technique of the Estimation of Phosphoric Acid. The Application of Pregl's Method in Serum Analysis. Stella Wiener (*Biochem. Zeitsch.*, 1921, **115**, 42—45).—The protein of the serum is removed with a mixture of picric and acetic acids and the phosphorus estimated by Pregl's method. The "lipoid" phosphorus is estimated in the precipitated residue after it has been incinerated. It can also be estimated by difference by subtracting the phosphorus content as estimated after precipitation of the protein from the total phosphorus estimated by incinerating the whole serum. S. S. Z.

Volumetric Estimation of Arsenious Compounds by Means of Potassium Dichromate. R. Meurice (*Ann. Chim. Anal.*, 1921, **3**, 85—86).—Hydrochloric acid and potassium bromide are added to the arsenious acid solution and the mixture is titrated with standardised dichromate solution; during the titration, a current of air is bubbled through the mixture and then through potassium iodide–starch solution contained in a test-tube. When all the arsenious acid has been oxidised, the next drop of dichromate solution added liberates bromine, which is carried over into the potassium iodide and a blue coloration develops in the latter. W. P. S.

The Separation and Detection of Arsenate and Arsenite. George W. Sears (*J. Amer. Chem. Soc.*, 1921, **43**, 466—470).—Determinations of the solubility of silver arsenate and silver arsenite respectively in sodium hydroxide solution show that, whereas the former is readily dissolved in the cold by 0·5 to 1·5*N*-sodium hydroxide, the latter is practically insoluble. The arsenate dissolves according to the equation $2Ag_3AsO_4 + 2NaOH + H_2O = 2NaH_2AsO_4 + 3Ag_2O$. Higher concentrations of sodium hydroxide react slowly with silver arsenite with formation of arsenate and precipitation of metallic silver. To separate arsenate and arsenite, their nitric acid solution containing excess of silver nitrite is neutralised with sodium hydroxide until the silver oxide precipitate just fails to redissolve. The washed precipitate is then shaken with about 25 c.c. of a solution containing about 3 c.c. of 6*N*-sodium hydroxide solution. This is sufficient to dissolve at least 0·45 gram of silver arsenate. The arsenate and arsenite can be detected in the filtrate and residue respectively by the usual methods. E. H. R.

Rapid Dry Combustion Method for the Simultaneous Determination of Soil Organic Matter and Organic Carbon. J. W. READ (*J. Ind. Eng. Chem.*, 1921, **13**, 305—307).—By means of Levene and Bieber's rapid combustion method (A., 1918, ii, 130), and with the aid of a combustion boat with a perforated base and a special filter funnel, the organic matter and the organic carbon may be estimated simultaneously. T. H. P.

Estimation of Carbon Dioxide in Air. JULIUS FREUND (*Zeitsch. Hyg.*, 1920, **91**, 218—222; from *Chem. Zentr.*, 1921, ii, 385—386).—Two simplified modifications of the Pettenkoffer method are described. In the first, a weak solution of sodium hydroxide is mixed with barium chloride solution in the flask, shaken with air, and a portion of the filtrate titrated with phenolphthalein as indicator.

The second method, which gives results in agreement with the Pettenkoffer method, is carried out as follows: 180 or 190 c.c. of distilled water, 5 c.c. of phenolphthalein and 20 to 10 c.c. of $N/10$-sodium hydroxide are placed in the flask filled with the air under examination. The stoppered flask is then shaken for twenty minutes and two portions of 50 c.c. are titrated with phenolphthalein as indicator. The difference between the titre thus obtained and a blank titration when multiplied by $4 \times 2{\cdot}24$ gives the carbon dioxide in c.c. at N.T.P. G. W. R.

The Estimation of Silicon in Cast Iron. EDUARDO D. GARCÍA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 40—52).—A review of the various methods used for the estimation of silicon in cast iron. G. W. R.

Estimation of the Alkalinity and of Phosphates in the Ashes of Foods. J. TILLMANS and ANNA BOHRMANN (*Zeitsch. Nahr.-Genussm.*, 1921, **41**, 1—17).—The alkalinity is estimated by boiling a portion of the ash with an excess of standardised acid, then adding 30 c.c. of 40% calcium chloride solution, and titrating the excess of acid, using phenolphthalein as indicator. Another portion (at least 0·2 gram) of the ash is boiled for one hour with 100 c.c. of $N/10$-hydrochloric acid, cooled, and titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator (c.c. of $N/10$-acid used equal B); 20 c.c. of saturated sodium oxalate solution are now added and the titration is continued, using phenolphthalein as indicator (c.c. of alkali used equal C). Then, if A is the number of c.c. of $N/10$-acid required to neutralise the alkalinity of the ash, the amount of orthophosphate, Y (mg. of PO_4), in the weight of ash taken is $3/2(B-A) \times 3{\cdot}167$; if the ash is not alkaline and C is a positive value, the orthophosphate is found by the formula $Y = 3C \times 3{\cdot}167$, and the pyrophosphate, Z, equals $2(B-2C) \times 4{\cdot}75$. When C has a negative value, pyro- and meta-phosphates are present; in this case, Z equals $2B \times 4{\cdot}75$, and the metaphosphate, U, equals $-C \times 9{\cdot}5$. W. P. S.

Centrifugal Method for Estimating Potassium. ELMER SHERRILL (*J. Ind. Eng. Chem.*, 1921, **13**, 227—228).—Five c.c. of a solution of the potassium salt (containing about 1% of K_2O)

are mixed in a centrifugal tube with 17 c.c. of sodium cobaltinitrite solution; a similar mixture is made in another tube, using in this case a solution containing a known amount of potassium. Both tubes are submitted to centrifugal action; the volumes of the precipitates are noted and a simple calculation gives the amount of potassium in the test solution. W. P. S.

The Przibylla Tartrate Method for Potassium. E. BORSCHE (*Kali*, 1920, **14**, 275—280, 303—308, 358—361, and 374—382; from *Chem. Zentr.*, 1921, ii, 476).—It is shown that the precipitation of potassium by tartaric acid, filtration, and titration of the excess of tartaric acid in the filtrate, is employable as a works method, provided that the accompanying material is not too variable in composition. Tables are usually given for salts of 80% or higher grades. For fertiliser salts of 20 to 40% grade special tables must be made to allow for deviations caused by the differing content of the other salts present. G. W. R.

New Method for the Estimation of Potassium in Silicates. JEROME J. MORGAN (*J. Ind. Eng. Chem.*, 1921, **13**, 225—226).—The silicate is decomposed by treating it with hydrofluoric acid at the ordinary temperature; a small quantity of dilute hydrochloric acid is then added and the mixture evaporated with the addition of perchloric acid; the residue is dissolved in water, and the evaporation repeated with the addition of a further quantity of perchloric acid. The potassium perchlorate formed is collected, washed, dried, and weighed in the usual way. Sodium and calcium sulphates interfere, since these are insoluble in alcohol containing perchloric acid, and their presence necessitates an estimation of sulphate in the weighed potassium perchlorate precipitate.
W. P. S.

Soil Reaction. II. The Colorimetric Determination of the Hydrogen-ion Concentration in Soils and Aqueous Soil Extracts. E. A. FISHER (*J. Agric. Sci.*, 1921, **11**, 45—65. Compare this vol., i, 215).—Details are given of the colorimetric method of determining hydrogen-ion concentration in a comparator as applied to soil extracts, the preparation of the requisite standard buffer solutions and the indicator solutions being given. For the determination of lime-requirements, increasing amounts of barium hydroxide are added to the soil before making the extract, the hydrogen-ion concentration is determined in each case, and a curve plotted. By interpolating at $-\log[H^{\cdot}] = 7{\cdot}07$ and calculating barium hydroxide into calcium oxide, the lime requirement is obtained. It is shown that fineness of division of the soil is an important factor in these soil acidity determinations. W. G.

Estimation of Calcium and Magnesium in Different Saline Solutions. E. CANALS (*Bull. Soc. Chim.*, 1921, [iv], **29**, 152—158. Compare A., 1920, ii, 193, 708).—Magnesium is not precipitated along with the calcium oxalate if the dilution of the magnesium ion is greater than 1‰. If owing to higher concentrations some

of the magnesium is precipitated, it may be removed by repeated washing with boiling water, 500 c.c. being necessary in some cases.

W. G.

[**Estimation of Thallium as Chromate.**] V. CUTTICA and G. CANNERI (*Gazzetta*, 1921, **51**, i, 169—174).—See this vol., i, 322.

Electro-analytical Separation of Copper, Antimony, and Tin. F. FOERSTER and D. AANENSEN (*Zeitsch. Elecktrochem.*, 1921, **27**, 10—16).—The method of electro-analysis of copper–tin alloys, containing about 5—10% of antimony, put forward by Schurmann and Arnold (A. 1908, ii, 898) has been examined and found to be thoroughly trustworthy. The authors describe a method of separation of these elements, with full working details. The solution is made by dissolving 0·04—0·05 gram of antimony in a little nitric acid and tartaric acid, 50 c.c. of a solution of copper nitrate are added, and the whole is evaporated to dryness. Five c.c. of nitric acid (D 1·4), 5 c.c. of 50% tartaric acid, 10 c.c. of stannous sulphate solution, and sufficient hydrogen peroxide to oxidise the latter, are added and the whole is made up to 40 c.c. This solution is electrolysed, with strong cooling, for an hour with a current of 1·5 amperes in a Frary apparatus with a 5-ampere coil current. The copper deposit is carefully removed from the cathode with nitric acid and tartaric acids and the copper redeposited in the same manner. Since the first deposit contains no tin but only antimony as impurity, the two solutions, after the second deposition of copper, are not mixed, but each is neutralised with sodium hydroxide, treated with 50 c.c. of 10% oxalic acid and also treated hot with hydrogen sulphide. The two antimony precipitates are united, dissolved in alkali sulphide, and the solution is treated as follows. To the solution, 30 c.c. of 30% potassium cyanide solution are added and the mixture is electrolysed at 70° with 0·6 ampère, using a Winkler net electrode. The deposition requires about two hours for 0·1 gram of antimony and the deposit is 1·8% heavier than the quantity of antimony present. The solution containing the tin is concentrated, neutralised with 50% potassium hydroxide, made alkaline with 2 c.c. of 50% potassium hydroxide solution, treated with 1· c.c. of 3% hydrogen peroxide, and boiled and diluted to 150 c.c. The tin is then deposited in three and a half hours at 80—85° on a Winkler electrode with a current of 5 ampères; during the electrolysis, 3 c.c. of 50% potassium hydroxide is added along with water to make good the evaporation. The method gives remarkably good results. J. F. S.

Detection of Mercury as Cuprous Mercuric Iodide. P. ARTMANN (*Zeitsch. anal. Chem.*, 1921, **60**, 81—88).—When a drop of a mercury salt solution is placed on a strip of filter-paper which has been coated with cuprous iodide and dried, a bright red coloration is obtained; the test may also be carried out on a microscopic slide. The reaction may be obtained with a solution containing 2 mg. of mercury per litre. Bismuth salts, and substances which are reduced readily, must not be present, and the acidity of the mercury solution should not be greater than $N/10$. W. P. S.

Electrolytic Separation of Mercury and Copper. W. Böttger (*Zeitsch. angew. Chem.*, 1921, **34**, 120—122).—For the removal of mercury and copper from a solution containing chlorine ions, 80 c.c. of the solution with 4 c.c. of nitric acid (D 1·4) and 3 c.c. of alcohol are electrolysed at an initial voltage of 2·2 volts, with a current of 3 amperes which drops to 1·5 amperes in three to five minutes. After separation of the mercury, the voltage is increased to 2·4 volts, the current increasing to 2·6 amperes, and copper is then separated in ten to fifteen minutes. After weighing the deposit, it is dissolved in nitric acid (D 1·2), diluted with an equal quantity of water, neutralised with ammonia, and, after addition of acid and alcohol, electrolysed at 1·4 volts. In Goecke's method, using potassium cyanide, the addition of concentrated ammonia before adding potassium cyanide prevents decomposition of the latter during electrolysis. A voltage of 2·9 volts, rising to 3 volts, is employed, and satisfactory results are obtained in twenty minutes. Separation of copper from 100 c.c. of a solution containing 5 c.c. of ammonia and 5 grams of potassium cyanide is effected at normal temperature with 3·2 volts, whilst without ammonia the necessary voltage is 3·8—4·5 volts. At 65°, an appreciably lower voltage, approximately 2 volts, may be employed.

W. J. W.

Principles of Analysis by Means of Reducing Flames; Detection of Traces of Manganese in the Presence of Iron or other Substances. Jean Meunier (*Compt. rend.*, 1921, **172**, 678—681).—When an oxide or a salt, introduced into a flame, undergoes a reduction there, that reaction is manifested by a line spectrum. If the oxide is not reduced, the spectrum of the metal is not produced, but only a continuous spectrum of incandescence. It is necessary in many cases to use a hydrogen flame, as its reducing action is more energetic than that of a gas flame. In this method manganese is characterised by the triplet, 4034·7, 4033·2, 4030·9, which is of extraordinary sensitiveness. W. G.

Estimation of Small Quantities of Iron in Organic Liquids, Especially in Wines. P. Malvezin and Ch. Rivilland (*Ann. Chim. anal.*, 1921, **3**, 90—92; *Bull. Soc. chim.*, 1921, [iv], **29**, 237—239).—The method depends on the titration of ferric salts with thiosulphate solution, sodium salicylate being used as indicator and copper sulphate as catalyst in the reduction. For example, the ash from 20 c.c. of wine is dissolved in 10 c.c. of 5% hydrochloric acid, the solution filtered, and treated with 0·5 c.c. of hydrogen peroxide; after fifteen minutes, the mixture is boiled to decompose excess of hydrogen peroxide, 5 c.c. of 1% copper sulphate solution and 1 c.c. of 2% sodium salicylate solution are added, and the mixture is titrated with standardised thiosulphate solution, the end point being denoted by the disappearance of the violet coloration. W. P. S.

Method of Separating Ferric, Aluminium, and Chromium Hydroxides. (Mme) M. Lemarchands and M. Lemarchands (*Ann. Chim. anal.*, 1921, **3**, 86—87).—The mixed precipitated

hydroxides are washed until free from ammonia and then boiled with 10% sodium hydroxide solution containing sodium perborate. The ferric hydroxide remains insoluble and is separated by filtration, whilst aluminium and chromium are found in the filtrate as sodium aluminate and sodium chromate. The aluminium may be separated by boiling a portion of the filtrate with an excess of ammonium chloride, and in another portion of the filtrate the chromium may be precipitated as lead chromate. W. P. S.

A New Method for the Detection and Estimation of Cobalt. S. A. Braley and F. B. Hobart (*J. Amer. Chem. Soc.*, 1921, **43**, 482—484).—It was noticed when testing for nickel with dimethylglyoxime that, when cobalt was present, a brown coloration resulted. This coloration has been found to be characteristic for cobalt, since, unlike the colour given by other metals, it is not discharged by mineral acids. It provides a sensitive test for cobalt in the absence of copper and iron. Since the depth of colour is proportional to the concentration, it can be used as a colorimetric method for the estimation of cobalt. For this purpose the cobalt dimethylglyoxime solution must be acidified with acetic acid and sodium acetate. E. H. R.

Cyanometric Assay of Nickel. G. H. Stanley (*J. S. African Assoc. Anal. Chem.*, 1921, **4**, 10—12).—The ammoniacal solution of the nickel salt is titrated with potassium cyanide solution, the end-point being denoted by the disappearance of the precipitate first formed. The end-point may be rendered sharper by adding a known amount of silver nitrate and a small quantity of potassium iodide, an allowance being made for the amount of added silver. If iron is present, the nearly neutral solution must be treated with an excess of cyanide, then rendered ammoniacal, filtered, the excess of cyanide titrated with silver nitrate solution in an aliquot portion of the filtrate, and the nickel estimated by difference. Copper must be removed previously, zinc may be removed by using sodium carbonate in place of ammonia for precipitating the iron, and cobalt is estimated together with the nickel; manganese does not interfere if ammonium chloride is added. Molybdenum tends to interfere if the titration is delayed. W. P. S.

Iodometric Method for the Estimation of Chromium in Chromite. Ernest Little and Joseph Costa (*J. Ind. Eng. Chem.*, 1921, **13**, 228—230).—A quantity of 0·4 gram of the chromite is fused in an iron crucible with 5 grams of sodium peroxide, the mass then dissolved in water, the solution treated with a further 0·5 gram of peroxide, and boiled to decompose the excess of the latter. The solution is then cooled, hydrochloric acid added until all ferric hydroxide has dissolved, 5 c.c. of concentrated hydrochloric acid per 100 c.c. of solution are introduced, followed by an excess of ammonium fluoride, and, after the addition of potassium iodide, the liberated iodine is titrated with standardised thiosulphate solution. W. P. S.

The Carrying Down of Lime and Magnesia by Precipitates of Chromic Oxide. ER. TOPORESCU (*Compt. rend.*, 1921, **172**, 600—602).—In the precipitation of chromium from solutions of its salts by ammonium hydroxide, when calcium or magnesium salts are present, the author finds that the amounts of calcium or magnesium carried down increase with the concentration of their salts present tending towards a limit corresponding with the chromites $Cr_2O_3,3CaO$ and $Cr_2O_3,3MgO$ respectively. The whole of the calcium may be removed by washing the precipitate on the filter with a boiling 5% solution of ammonium nitrate, whilst the magnesium is best removed by washing the precipitate by decantation with a similar solution. W. G.

Separation of Tin and Antimony in Hydrochloric Acid Solution by Means of Hydrogen Sulphide. G. LUFF (*Chem. Zeit.*, 1921, **45**, 229—231).—The effect of temperature, solution, concentration, etc., on the precipitation of antimony and tin sulphides was investigated. When a solution of antimony or tin containing 30 c.c. of concentrated hydrochloric acid is heated and treated with hydrogen sulphide, precipitation of the antimony sulphide begins at 80°, whilst the tin sulphide remains in solution even when the mixture is cooled to 25°. Ammonium chloride has a somewhat similar influence on the precipitation. W. P. S.

Separation of Tin and Antimony in Hydrochloric Acid Solution by Means of Hydrogen Sulphide. G. LUFF (*Chem. Zeit.*, 1921, **45**, 249—251, 254—255, 274).—The effect of adding increasing amounts of concentrated hydrochloric acid to boiling solutions of antimony and tin salts into which hydrogen sulphide is passed, is to lower the temperature at which precipitation occurs. With 30 c.c. per 100 c.c. of solution, separation of antimony trisulphide takes place at 95°; of the pentasulphide at 80°; and of stannic sulphide at 25°. Addition of 36 grams of ammonium chloride lowers the temperature at which precipitation is effected to 78° and 60°, respectively, with the trisulphide and pentasulphide of antimony; in the case of tin, no precipitation occurs even at normal temperature, until the solution has been allowed to remain. The best separation is realised with an addition of 14 c.c. of concentrated hydrochloric acid (D 1·193) to 100 c.c. of solution; the maximum and minimum concentrations are found to be 35 c.c. per 65 c.c. and 8 c.c. per 100 c.c. of solution. Vortmann-Metzel's and Panajotow-Prim's methods both give accurate results in the separation of antimonious salts. W. J. W.

Behaviour of Sodium Thioantimonate with certain Metallic Salt Solutions. A. LANGHANS (*Zeitsch. anal. Chem.*, 1921, **60**, 91—93).—Sodium thioantimonate solution yields the following reactions with various metallic salt solutions :—Aluminium, chromium, manganese, orange-red precipitates; zinc, cadmium, yellow precipitates; iron, nickel, cobalt, bismuth, black precipitates; silver, copper, lead, reddish-brown precipitates. With mercury salts, the coloration of the precipitate varies with the

salt; mercuric oxalate, mercuric oxide, and mercurous nitrate are blackened, whilst mercuric bromide gives a yellow precipitate. Mercuric cyanide yields a yellow precipitate which changes to black, and mercuric chloride gives a red precipitate which gradually changes to white. Mercury fulminate is at first coloured yellow, but this colour soon changes to green and finally to black. Mercury potassium iodide yields an orange-coloured, flocculent precipitate.

W. P. S.

The Estimation of Gold by Cupellation and the Examination of Large Quantities of Gold Destined for the Manufacture of Coinage. J. W. A. Haagen Smit (*Rec. trav. chim.*, 1921, **40**, 119—152).—A critical and detailed examination of the cupellation method for the analysis of gold bullion in which the author lays down certain details to which strict attention must be paid if accurate results are to be obtained. [See further *J. Soc. Chem. Ind.*, 1921, 263A.]

W. G.

Application of the Critical Temperature of Solution in Aniline to the Analysis of Light Petroleums. G. Chavanne and L. J. Simon (*Ann. Chim. anal.*, 1921, **3**, 87—89).—The critical temperature of solution of the sample in aniline is determined, before and after the sample has been treated with a mixture of sulphuric and nitric acids and then washed with sulphuric acid to remove the nitrated aromatic hydrocarbons. The following formulæ then give the approximate composition of the petroleum: Aromatic hydrocarbons $(Ar)=1{\cdot}18(T_2-T_1)$; saturated cyclic hydrocarbons $(C)=72-(T_2-0{\cdot}2)/72-39{\cdot}5\times(100-Ar)$; acyclic hydrocarbons $(Ac)=100-Ar-C$, where T_1 and T_2 are the critical temperatures of solution before and after nitration respectively.

W. P. S.

Estimation of Benzene Hydrocarbons in Coal Gas. E. Berl, Karl Andress, and Wilhelm Müller (*Zeit. angew. Chem.*, 1921, **34**, 125—127).—An accurate method for estimating benzene hydrocarbons in coal gas, even when present in only small amount, consists in adsorbing them by charcoal, and then distilling them in steam. The apparatus consists of a U-tube, widened at its lower half, and having inlet- and outlet-tubes with taps fixed in its open ends. A layer of dry charcoal is placed in the tube over which the gas to be tested is passed, at a rate dependent partly on the content of benzene hydrocarbons, but approximately of 250 litres per hour. When adsorption is complete, one limb of the tube is connected with a steam supply, and to the other limb are attached a condenser and measuring burette; the tube is heated in a bath to 110—120°, in a current of steam, for about thirty minutes, and the distilled benzene hydrocarbon layer is measured. More accurate results are obtained by this method than by either the dinitrobenzene or the paraffin oil method; thus the proportion of benzene hydrocarbons in a sample of illuminating gas was found to be 20·2—23·9 c.c. per cub. m., as compared with 16·0—17·2 and 9·74—10·1 c.c. per cub. m., respectively, by the other two methods.

W. J. W.

A Sensitive Modification of the Iodoform Reaction for Alcohol. N. SCHOORL (*Pharm. Weekblad*, 1921, **58**, 209—210).—Instead of potassium persulphate in presence of potassium iodide in alkaline solution, as suggested by Kunz (A., 1920, ii, 711), ammonium persulphate may be employed. The iodoform precipitate is in this case orange to red, without crystalline form, but passes into the yellow, crystalline modification after several days. In the new form, the reaction will detect one part of acetone in 100,000. S. I. L.

Rapid Volumetric Method for Estimating Ethyl Alcohol. ARTHUR LACHMAN (*J. Ind. Eng. Chem.*, 1921, **13**, 230).—To estimate the amount of ethyl alcohol in a water–alcohol mixture, 25 grams of aniline are added to 50 c.c. of the mixture; if the aniline does not dissolve completely, a known amount of alcohol must be added. The whole mixture is then titrated with water until a permanent turbidity is produced. During the addition of the water the temperature is kept at about 15°. The total volume of the solvent (alcohol plus water) is a nearly strictly linear function of the volume of the alcohol present; the latter volume is found by reference to a graph constructed from the results of estimations in which known amounts of alcohol were used. W. P. S.

Estimation, by Acetylation, of Borneol and its Acylated Derivatives. FÉLIX MARTIN (*J. Pharm. Chim.*, 1921, [vii] **23**, 168—171).—Borneol may be converted completely into bornyl acetate by heating it at 145—150° for three hours with three times its weight of acetic anhydride and a small quantity of fused sodium acetate. After cooling, the mixture is diluted with water, the oily layer separated, washed with water, then with 5% sodium carbonate solution, again with water, and dried over anhydrous sodium sulphate. A weighed quantity of the acetylated substance is then saponified and the quantity of borneol calculated from the saponification value, allowance being made for the fact that the acetylation increases the molecular weight of the borneol by 42. W. P. S.

Sodium Fluoride or Citrate as Anti-coagulant in Estimating Blood Sugar. R. CLOGNE and A. RICHAUD (*Bull. Soc., Chim. Biol.*, 1921, **3**, 66—68).—With citrate, blood glycolysis continues and after twenty-four hours scarcely any sugar is left, but when coagulation is prevented by sodium fluoride, satisfactory results are obtained, even after four days. G. B.

Estimation of Maltose or Lactose in the Presence of other Reducing Sugars (use of Barfoed's Solution). LEGRAND (*Compt. rend.*, 1921, **172**, 602—604).—Barfoed's solution of copper acetate and acetic acid (this Journal, 1873, 1163) is reduced by hexose-sugars but not by the disaccharides. Estimations of hexose-sugars are best conducted by boiling 5 c.c. of the sugar solution, containing at the most 0·1 gram of sugar, with 15 c.c. of Barfoed's solution for three minutes in a conical flask, the cuprous oxide being subsequently collected and estimated volumetrically as in

Bertrand's method. If disaccharides are present, the total reducing sugars are then estimated by one of the usual methods with Fehling's solution. W. G.

Polarimetric Estimation of Starch. H. LÜHRIG (*Pharm. Zentr.-h.*, 1921, **62**, 141—144).—Ewer's method (A., 1908, ii, 543) yields trustworthy results, and the latter are not influenced to any great extent by slight differences in the procedure, particularly as regards the concentration of the acid. It is most important, however, that the time of heating (fifteen minutes) should not be altered, and in no case should it exceed sixteen minutes. A method described recently by Mannich and Lenz (Zeitsch. Nahr. Genussm., 1920, **40**, 1), in which the starch is dissolved in hot calcium chloride solution containing a small quantity of acetic acid, also yields trustworthy results. W. P. S.

Detection of Lactic Acid. L. HARTWIG and R. SAAR (*Chem. Zeit.*, 1921, **45**, 322).—A bright red coloration is obtained when 0·2 c.c. of a solution containing not more than 0·2% of lactic acid is heated for two minutes at 100° with 2 c.c. of concentrated sulphuric acid, then cooled, and treated with 2 drops of 5% alcoholic guaiacol solution. The reaction is not given by formic acid, acetic acid, malic acid, benzoic acid, or salicylic acid; citric acid gives a yellow coloration and tartaric acid a slight red coloration, whilst tannin yields a blackish-violet colour. W. P. S.

Estimation of Oxalic Acid and Oxaluric Acid in Urine and in Fæces. ARMINIUS BAU (*Biochem. Zeitsch.*, 1921, **114**, 221—257).—For the estimation of oxalic acid in urine, the clear solution is digested with a mixture of sodium acetate and calcium chloride for thirty-eight to forty-four hours, the calcium oxalate is then collected, incinerated, and titrated with $N/10$-hydrochloric acid. In order to estimate the oxaluric acid content of the urine, the oxalic acid is first estimated as described above, and then another portion is boiled for an hour with hydrochloric acid (D 1·125), filtered, nearly neutralised with ammonia and treated with the sodium acetate and calcium chloride mixture. The oxalic acid is then estimated in the same way as before. The difference between the oxalic acid obtained after the treatment with the hydrochloric acid and the original content of oxalic acid gives the oxaluric acid content of the urine. The fæces are dried, extracted with water and hydrochloric acid, filtered, and in the filtrate, after neutralisation with ammonia and treatment with ammonium citrate, the oxalic acid is estimated as above. S. S. Z.

Identification of Acids. VI. Separation of Acids by Means of Phenacyl Esters. J. B. RATHER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 629—636).—In continuation of previous work (A., 1920, i, 381), a number of illustrations chosen from naturally occurring organic acids are given to show that the constituents of a mixture of such acids may frequently be identified by preparation of their phenacyl esters from the sodium salts, followed by fractional crystallisation. J. K.

The Detection of Methyl Anthranilate in Fruit Juices. FREDERICK B. POWER (*J. Amer. Chem. Soc.*, 1921, **43**, 377—381).—Five hundred c.c. of the juice are steam distilled, 200 c.c. of distillate being collected. The distillate is extracted with three successive 10 c.c. of chloroform, the extract being passed through a dry filter and the chloroform carefully evaporated on a water-bath in a current of air. The residue is at once dissolved in 2 c.c. of 10% sulphuric acid, the solution cooled, and one drop of a 5% solution of sodium nitrite is added, the excess of nitrous acid being subsequently destroyed by the addition of carbamide. The diazotised solution is added to a mixture of 1 c.c. of 0·5% β-naphthol solution, 1 c.c. of 10% sodium hydroxide, and 1 c.c. of 10% sodium carbonate (monohydrated). A yellowish-red precipitate is obtained if methyl anthranilate was originally present in the juice, the test being sensitive to 0·0001 gram of the ester. Alternatively, the diazotised liquid may be tested with dimethylaniline, but this is not so sensitive as the β-naphthol. W. G.

Detection of Acetone by Degradation to Derivatives of Formic Acid. EMILIO PITTARELLI (*Policlinico*, 1920, **27**, 1047—1049; from *Chem. Zentr.*, 1921, ii, 536).—Acetone is converted by chlorine, bromine, or iodine in strongly alkaline solution into chloroform, etc. Excess of free halogen is removed and the haloid is detected by warming with phenol and subsequent heating with alkali hydroxide, by the carbylamine reaction, or by reduction to acetylene (with zinc and ammonium chloride). H. W.

Colour Reaction of Indones. REMO DE FAZI (*Gazzetta*, 1921, **51**, i, 164—169).—The green coloration obtained by the action of concentrated sulphuric acid on various lactic and cinnamic acid derivatives is shown to be due to the formation from these derivatives of indones, which are capable of combining with sulphuric acid at the double linking of the cyclostatic group, ·CO·C:C—, giving intensely coloured compounds; the reaction is not shown by hydrindones. Further, it seems probable that indene derivatives of the type 2 : 3-diphenylindene containing the cyclostatic group, $·CH_2·C:CH$, also give the colour reaction with sulphuric acid. Since stable acids derived from cinnamic acid furnish no coloration, the reaction may be used to distinguish stable cinnamic acids from the allo-compounds. T. H. P.

Detection of "Saccharin." A Correction. L. THEVENON. (*J. Pharm. Chim.*, 1921, [vii], **23**, 215).—The author finds that a reaction he described recently (this vol., ii, 69) is not characteristic of "saccharin." β-Naphthol, one of the reagents used, yields a red coloration with nitrous acid in dilute acid solution, even in the absence of "saccharin." W. P. S.

Separation of *o*- and *p*-Toluenesulphonamides. WALTER HERZOG and I. KREIDL (*Chem. Zeit.*, 1921, **45**, 231).—Separation of the two sulphonamides, as proposed by O. Beyer, by means of 10% sulphuric acid is not possible; both the sulphonamides are soluble in this acid. If, however, *o*-sulphonamide containing not

more than 2% of *p*-sulphonamide is dissolved in hot 10% sulphuric acid and the solution cooled, the *p*-sulphonamide crystallises out, leaving the greater part of the *o*-sulphonamide in solution.

W. P. S.

Detection of Volatile Alkylamines in the Presence of Ammonia and of Volatile Tertiary Alkylamines in the Presence of Volatile Primary and Secondary Alkylamines. H. E. Woodward and C. L. Alsberg (*J. Biol. Chem.*, 1921, **46**, 1—7).—Incipient decomposition of foodstuffs may be recognised by the presence of traces of amines, which are, however, difficult to distinguish from the ammonia also present. In dilute alkaline solution, ammonia reacts with formaldehyde to form hexamethylenetetramine, but methylamines furnish methyl alcohol and formic acid. The formic acid is detected by a solution containing 180 grams of mercuric bromide and 120 grams of potassium bromide per litre, which gives, on warming, a white precipitate of mercurous bromide when 0·5 mg. of amine-nitrogen is present. Ammonia and mono- and di-methylamine also give a white precipitate with mercuric bromide, but this is soluble in excess of formaldehyde.

Trimethyl- and triethyl-amine form with potassium mercuric iodide (450 grams of HgI_2 and 330 grams of KI per litre) yellow, crystalline compounds melting at 136° and 77° respectively, if excess of potassium iodide is avoided. Trimethylamine is still precipitated at 3 mg. in 5 c.c.; dimethylamine requires to be at least six times as concentrated. At suitable concentrations the tertiary amine only is precipitated, and then may be obtained pure, by distilling the mercuri-iodide with sodium hydroxide and sulphide (compare Weber and Wilson, A., ii, 377; Bertheaume, A., 1908, ii, 742; 1910, i, 365; ii, 663, 808; François, A., 1904, i, 151; 1905, i, 574; 1906, i, 484, 644; 1907, i, 391; ii, 503). G. B.

A Colour Reaction of Glycine Anhydride and the Dipeptide Anhydrides containing Glycyl Components. Takaoki Sasaki (*Biochem. Zeitsch.*, 1921, **114**, 63—66).—Glycine anhydride, creatinine, and certain related compounds as well as many other substances give a colour reaction with picric acid when heated. In these reactions it is preferable to use sodium carbonate instead of alkali hydroxide. Substances which are slightly soluble in water are dissolved in alcohol and treated with alcoholic picric acid. The use of this colour reaction in the estimation of sugar may easily lead to error, especially in the case of minimal amounts of sugar in pathological blood samples. S. S. Z.

The Removal of Ammonia from Urine Preparatory to the Determination of Urea. Guy E. Youngburg (*J. Biol. Chem.*, 1921, **45**, 391—394).—The ammonia is removed by adsorption by permutite. (See Folin and Bell, A., 1917, ii, 268.) J. C. D.

An Improved Apparatus for Use in Folin and Wu's Method for the Estimation of Urea in Blood. Thomas Watson and H. L. White (*J. Biol. Chem.*, 1921, **45**, 465—466).—The apparatus is designed to counteract foaming during the distilla-

tion of the ammonia; the bulbed tube connecting the flask to the condenser projects some way below the cork, the end is constricted, and a number of small holes are blown in the side. In passing through these the large bubbles are broken up. J. C. D.

Non-protein Nitrogen of Human Blood. II. [The Satisfactory Estimation of the Urea Fraction.] JOH. FEIGL (*Zeit. ges. expt. Med.*, 1921, **12**, 55—133; from *Chem. Zentr.*, 1921, ii, 692).—The estimation of urea by the ordinary sodium hypobromite method cannot be depended on. The exact estimation of urea, which is of considerable importance in blood investigations, can only be effected by the urease and xanthydrol methods.

G. W. R.

Characteristic Reaction for the Detection of Mercury Fulminate. A. LANGHANS (*Zeitsch. anal. Chem.*, 1921, **60**, 93—94).—If mercury fulminate is moistened with alcohol, then with water, and shaken with sodium thioantimonate solution, a yellow precipitate is obtained; this becomes green and then black. The filtrate from this precipitate deposits white, glistening crystals and when treated with nitric acid yields a red coloration which is soluble in ether. W. P. S.

Detection of Small Quantities of Hydrocyanic Acid from Cyanogenetic Glucosides. G. DENIGÈS (*Compt. rend. Soc. Biol.*, **84**, 309—310; from *Chem. Zentr.*, 1921, ii, 623).—Hydrocyanic acid is detected by the formation of oxaluramide by the simultaneous action of ammonia and alloxan. The alloxan reagent is made by gently heating 1 gram of pure uric acid, 1 c.c. of nitric acid (D 1·39—1·40), and 1 c.c. of water until clear; 50 c.c. of water are then added. The substance under examination is mixed with an equal weight of water and left for one hour in a tall, narrow glass tube on the end of which is placed a watch glass carrying a drop of the above reagent. In the presence of hydrocyanic acid, a coloration is observed due to the presence of oxaluramide in a star-shaped crystals. The reaction is more delicate if pyridine is used in the place of ammonia. A red colour is often observed due to murexide formed by the action of dialuric acid (accompanying oxaluramide) on excess of alloxan. G. W. R.

Origin, Development, and Value of the Thalleioquinine Reaction. WM. BEAUMONT HART (*J. Soc. Chem. Ind.*, 1921, **40**, 72—73T).—The earliest published record of the green coloration produced by treating a quinine solution with chlorine and ammonia is made by Meeson (*Phil. Mag.*, 1835, 158) and the reaction has since been modified in various ways (substitution of bromine for chlorine, etc.). The author finds that excess of bromine is detrimental, the greatest depth of colour being given by 6 atoms of bromine per molecule of quinine; the reaction is very sensitive, the mit being 1 : 250,000 in a depth of 2·25 inches of solution, but with so many variables the reaction is untrustworthy for quantitative work. W. P. S.

Rapid Method for Estimation of Morphine in Opium and Opium Preparations. TRIFÓN UGARTE (*Anal. Soc. Quím. Argentina*, 1920, **8**, 268—270).—The alcoholic extract of the substance under examination is evaporated to dryness and maintained at 100° to render resins insoluble. After extraction with cold water, the residue from the evaporation of the filtrate is treated with a saturated solution of morphine and a normal solution of ammonia saturated with morphine. The resulting solution is shaken with successive portions of ether. Crystals of morphine are obtained in the aqueous portion. These are collected, washed with water saturated with morphine and ether, dried, and weighed.

G. W. R.

A Reaction to Distinguish between Theobromine and Caffeine. M. MALMY (*J. Pharm. Chim.*, 1921, [vii], **23**, 89—91).—The difference in the behaviour of theobromine bismuthoiodide, and the corresponding compound of caffeine towards the reducing action of hydriodic acid, may be used to differentiate between these two substances. The test is conveniently performed as follows: 0·05 gram of theobromine or caffeine is shaken with 10 c.c. of water and 0·5 c.c. of fresh potassium bismuthoiodide solution. In each case an orange-coloured precipitate is obtained, and 5 drops of a 10% tincture of iodine (not freshly prepared, so that it may contain a small proportion of hydriodic acid) are added. The caffeine bismuthoiodide precipitate changes in colour to a bright red, whilst the theobromine precipitate becomes brown in fifteen minutes, and dark chocolate brown in less than thirty minutes, owing to reduction. A dilute solution of hydriodic acid containing not more than 1% of hydrogen iodide may be used instead of the tincture of iodine if desired. G. F. M.

Estimation of Yohimbine in Yohimba Bark. ARNOLD SCHOMER (*Pharm. Zentr.-h.*, 1921, **62**, 169—171).—Fifteen grams of the powdered bark are shaken for ten minutes with 150 grams of ether, 10 grams of 15% sodium hydroxide are added, the mixture is shaken, and, after one hour, 100 grams of the ethereal solution are shaken with successive quantities of 1% hydrochloric acid. The acid extracts are shaken with 25 c.c. of chloroform, this is separated, the acid solution then rendered alkaline with sodium carbonate solution and extracted with chloroform; the chloroform extract is evaporated and the residue obtained is dissolved in a small quantity of alcohol and a few drops of hydrochloric acid, the alcohol is evaporated, 5 c.c. of ether are added, this is also evaporated, and the residue warmed with 50 drops of alcohol. After a further evaporation, which is carried almost to dryness, the crystalline residue is treated with 50 grams of chloroform, cooled at 0°, and the crystals are then collected, dried at 100°, and weighed. W. P. S.

Estimation of Amylase. L. AMBARD (*Bull. Soc. Chim. Biol.*, 1921, **3**, 51—65).—See this vol., i, 368.

General and Physical Chemistry.

Theory of Molecular Refractions. I. GERVAIS LEBAS (*Chem. News*, 1921, **122**, 194—196).—The relation between refractivity and valency is considered. Augmentation may be due both to substitution and to unsaturation. The activation of supplementary valencies may be due to the influence of unsaturated atoms other than carbon. Atoms of high atomic weight are more likely to activate one another than those of low, and the effects are greater when the atoms are united by an unsaturated group.
J. R. P.

Additive Properties of Salts of Organic Acids. MARÍA L. LECCE DE GARCÍA (*Ann. Soc. Quím. Argentina*, 1920, **8**, 381—392. Compare Bernaola, this vol., ii, 285).—The application of the law of moduli is less exact the more carbon atoms are contained in the acid radicle of a salt. Moduli obtained from the consideration of the properties of normal solutions cannot be used for the calculation of the properties of solutions of different concentrations. Additive properties are best exemplified in the case of the refractive indices of salts of the first three members of the fatty acid series. Specific refractive powers for salts containing less than a certain proportion of carbon (30 to 37·4%, according to the formula used for the calculation of this value) increase with decreasing concentration. Absolute refractive power increases in ascending an homologous series. The effect of constitution is very marked, the benzene nucleus having a much greater effect on refractive power than would be expected from its containing six carbon atoms. G. W. R.

The Specific Dispersion of Hydrocarbons. E. DARMOIS (*Compt. rend.*, 1921, **172**, 1102—1105).—The approximate constancy of the specific dispersion for each series of hydrocarbons, as determined experimentally (this vol., ii, 1) is now confirmed theoretically by calculation from the atomic refractions. The agreement is not quite satisfactory when the hydrocarbons contain one or more ethylenic linkings. W. G.

A Spectroscopic Confirmation of the Isotopes of Chlorine. A. KRATZER (*Zeitsch. Physik*, 1921, **4**, 476).—An addition to the author's previous paper (this vol., ii, 142) consisting of references to further work on the spectra of isotopes which had been done prior to the appearance of the author's paper. J. F. S.

The Iodine Molecule and the Emission of its Band Spectrum. W. STEUBING (*Ann. Physik*, 1921, **64**, [iv], 673—691).—The positive column of an iodine tube with carbon electrodes has been spectroscopically examined when under the influence of a magnetic field and other sources of energy. The influence of a magnetic field is

to produce a band spectrum in which the energy maximum is displaced toward longer wave-lengths. The band spectrum is to be attributed to the iodine molecule, since it can be produced by fluorescence without simultaneous ionisation and dissociation. It also appears when ionisation takes place if the exciting cause is one of small energy content, but if the energy content is great the band spectrum disappears and a line spectrum takes its place. The band spectrum is produced by the combination of a negative electron with the molecule. Hence, for the character of the spectrum, it is of no importance whether the electron comes from the molecule itself (fluorescence) or from outside as a free electron (cathode rays). In both cases the magnetic field accelerates the combination.

J. F. S.

Spectra of some Compound Gases in Vacuum Tubes. W. H. BAIR (*Astrophys. J.*, 1920, **52**, 301—316).—Photographic observations were made of the spectra of ammonia, nitrous oxide, nitrogen peroxide, carbon dioxide, hydrogen sulphide, and sulphur dioxide, a regular flow of the gas through the discharge tube being maintained. The well-known ammonia band in the visible spectrum is found to have two heads, each degraded in both directions; the differences between this band and that at λ 3371 Å. suggest that the latter may be due to some other compound. Both oxides of nitrogen show strongly the third positive group of nitrogen bands, observed from λ 1902 Å. to λ 3458 Å.; those at the more refrangible end depart from Deslandres's law. Of the two negative groups of carbon bands, the first is probably due to carbon monoxide and the second, including several new bands, to carbon dioxide. The spectrum of sulphur dioxide is extended to λ 2124 Å. by the tabulation of forty new bands.

CHEMICAL ABSTRACTS.

Spectrum of Helium in the Extreme Ultra-violet. HUGO FRICKE and THEODORE LYMAN (*Phil. Mag.*, 1921, [vi], **41**, 814—817).—By improved experimental methods a fairly strong line at 585 Å.U. has been located, the resonance potential of which, 21·2 volts, agrees with the results of Franck and Knipping. It is concluded that, apart from the lines at 1640 Å.U. and 1215 Å.U. belonging to the enhanced spectrum but of doubtful origin, only one line can be ascribed with certainty to helium in the extreme ultraviolet. Other lines described by different experimenters are probably due to impurities.

J. R. P.

Revision of the Series in the Spectrum of Calcium. F. A. SAUNDERS (*Astrophys. J.*, 1920, **52**, 265—277. Compare A., 1920, ii, 522).—Singlets and triplets, and their combinations in the calcium spectrum have been studied and extended. There are no known combinations of these with the doublets; the latter may be associated with a different vibrating mechanism, for example, Ca^+. The diffuse series of triplets exhibits curious anomalies. Four triple-series of each system were found, and three possible intersystem combination series.

CHEMICAL ABSTRACTS.

Vacuum Hot-spark Spectrum of Zinc in the Extreme Ultra-violet Region. R. A. SAWYER (*Astrophys. J.*, 1920, **52**, 286—300).—With the use of an apparatus consisting of an evacuated brass cylinder containing electrodes, grating, slit, and plate holder, and by sparking intermittently under specified conditions, eighty new lines were observed of wave-lengths between 316 Å. and 1400 Å., and about twenty between 1400 Å. and 2200 Å. ($\pm$ 0·5 Å).
CHEMICAL ABSTRACTS.

The Luminescence of Samarium. HORACE L. HOWES (*Physical Rev.*, 1921, **17**, 60—63).—The effect was investigated of previous heat treatment on the luminescence spectrum obtained from samarium oxide mixed with a large excess of lime at 20° by excitation with cathode rays. With fresh preparations pre-heated (*a*) at 200° there was no luminescence at all; (*b*) at 400°, but few regions of luminescence were observed; (*c*) at 600°, the luminescence was sufficiently bright for spectrum analysis; (*d*) at or above 1200° the spectrum was of maximum brilliance. Variation in the duration of heat treatment between one and three hours had no effect. The luminescence spectrum consists of bands of varying intensities, which, plotted to a frequency scale, can be resolved into nine series of constant frequency intervals varying slightly for different series. A table shows the wave-length and reciprocal of wave-length of each band, together with the relative intensity and series letter. No shift in the position of the bands could be measured, whether the specimen was heated at 600° or 3000°. This remarkable stability is not generally associated with a luminescent substance. The minimum temperature for thermo-luminescence was about 200°.
CHEMICAL ABSTRACTS.

The X-Ray Spectra of Tungsten. WM. DUANE and R. A. PATTERSON (*Physical Rev.*, 1920, **16**, 526—539. Compare this vol., ii, 145; A., 1920, ii, 2, 407; A., 1919, ii, 358 and 488).—Measurements are tabulated for the critical absorption wave-lengths of the *K* and *L* series and the emission wave-lengths of the *L* series. The assumption of Sommerfeld that if some of the orbits are elliptic in certain atoms and circular in others the *K* critical absorption frequency should be complex, is not confirmed. Also if this assumption is correct, the difference between the *K* absorption frequency and one of the *L* absorption frequencies should not be equal to a K_α emission frequency, whereas this equality is shown to exist. The experimental data accord with Sommerfeld's expression for the frequency of the *L* series doublet.
CHEMICAL ABSTRACTS.

Precision Measurements in the *L* Series of the Heavier Elements. DIRK COSTER (*Zeitsch. Physik*, 1921, **4**, 178—188).—The lines of the *L* series spectrum have been measured for the elements tungsten, osmium, iridium, platinum, gold, thallium, lead, thorium, bismuth, and uranium by Siegbahn's method. The results are tabulated and show the presence of a new *L* doublet (β_6 and γ_5). The value of β_6 has been determined in the case of five of the elements and a tungsten line, noted by Siegbahn as doubtful, fits into this new

doublet very well. In the case of platinum, β_6 must fall very near to β_4, so that the existence of β_6 can be taken as known for seven elements. The intensity of β_6 lies between that of β_4 and β_5. The harder constituent, γ_5, is much weaker and has an intensity less than that of γ_4. In the case of platinum, gold, and thallium, a softer and very weak line, β_7, is found. It is also shown that the Λ-doublet does not exist. There is a possibility that an exact additive relationship exists between K_{β_1}, K_{β_2} and M_β. J. F. S.

Spark Spectra of Gold and Platinum in the Extreme Ultra-violet. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1921, **172**, 962—964).—The spark spectra of gold over the range $\lambda=1850$ to 1401 and of platinum over the range $\lambda=1843$ to 1461 are given. W. G.

The Effect of Fluorescence and Dissociation on the Ionising Potential of Iodine Vapour. H. D. SMYTH and K. T. COMPTON (*Physical Rev.*, 1920, **16**, 501—513. See A., 1920, ii, 723).—Since fluorescence is not accompanied by ionisation, it presumably results from the temporary displacement of an electron to one of the outer orbits; if this is so, less work should be required to ionise a fluorescing than a normal atom or molecule. In the curve obtained with fluorescing iodine vapour, three breaks are observed, occurring (*a*) at 6·42 volts, attributed to the ionisation of fluorescing iodine molecules; (*b*) at 7·67 volts, attributed to the ionisation of iodine atoms, and (*c*) at 9·07 volts, presumably due to the ionisation of normal, unexcited, diatomic iodine vapour. The mean difference between the values of (*a*) and (*c*) should be equal to the difference in the work needed to remove an electron from a fluorescent and a normal molecule; this value has previously been theoretically determined at about 2·3 volts. In the ionisation curve of unexcited atomic iodine, breaks occur at (*b*) 8·7 volts and (*c*) 10·16 volts, or an average value for all experiments of (*b*) 8·0 volts and (*c*) 9·4 volts, from which it is inferred that ionisation of the iodine molecule is accompanied by dissociation, as predicted by Bohr's theory for hydrogen and previously observed by Mohler and Foote (A., 1920, ii, 464) and by Franck, Knipping, and Krüger (A., 1920, ii, 145). The results are in accord with the view of Perrin (A., 1919, ii, 177) that quanta of radiant energy are emitted or absorbed in all chemical reactions. CHEMICAL ABSTRACTS.

Connexion between the Colour of Chemical Compounds and the Structure of the Molecule. JAKOB MEISENHEIMER (*Zeitsch. physikal. Chem.*, 1921, **97**, 304—318).—The author, on the basis of Kossel's hypothesis of the dependence of molecule formation on atomic structure (A., 1916, ii, 243), has put forward an hypothesis to explain why the chlorides of metals and the hydrochlorides of organic bases are so often white, whilst the corresponding iodides and hydriodides vary in colour from yellow to red. According to Kossel's hypothesis, when sodium combines with chlorine to form sodium chloride, the former element gives up its single valency electron to the chlorine, and the chlorine then, by

means of its own seven valency electrons and the electron from the sodium, takes up a form similar to an inactive gas. But iodine having a larger atomic volume than chlorine, and therefore a smaller attractive force between the nucleus and the outside electron sheath, is unable to take an eighth electron into its outer sheath from a metal in the same way as chlorine. Hence an irregular sheath of electrons is formed which is so unstable that the feeble energy of visible light is able to displace the electrons from their paths and so the compound must be coloured. In the same way, the author considers that the yellow and red varieties of mercuric iodide are isomeric because the iodine valency electrons possess different orbits. J. F. S.

Colour and Chemical Constitution. XI. A Systematic Study of the Brominated Phenolphthaleins regarding the Relation between Position and Colour. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1921, **9**, 129—136. Compare this vol., p. ii, 6).—The general formula previously derived (A., 1920, ii, 573) reduces, in the case of bromophenolphthaleins, to the form $\lambda=554+7\cdot091(m+0\cdot091m^2)$, m being the number of ortho-bromine atoms; in the case of meta-bromine atoms, m is to be doubled. Experimental data for five mono-, five di-, three tri-, two tetra-, three penta-, four hexa-, and one hepta-bromophenolphthaleins are shown to be usually within one unit of the values calculated from the above formula, together with additive coefficients which are given for substituents to which it does not apply. New monochloro- ($\lambda=564$) and monoiodo- ($\lambda=568\cdot5$) -phenolphthaleins derived from the meta-halogenated phenols were also examined. The negative effect of the para-substituent previously noted in the case of benzaurine derivatives, is not observed in the phenolphthalein series, and it is therefore suggested that the usual formulæ for phenolphthalein and also fluorescein in alkaline solution require such amendment as will make them wholly phenolic in character, and not containing the $-CO_2Na$ grouping. J. K.

The Photochemical Reaction between Hydrogen and Chlorine and its Variation with the Intensity of the Light. EDWARD CHARLES CYRIL BALY and WILLIAM FRANCIS BARKER (T., 1921, **119**, 653—664).

Photochemical Transformations in the Triphenyl-methane Series and Photo-concentration Cells. I. LIFSCHITZ and CH. L. JOFFÉ (*Zeitsch. physikal. Chem.*, 1921, **97**, 426—444).—Solutions of the leuco-cyanides of pararosaniline, crystal-violet, victoria-blue, malachite-green, and brilliant-green and the carbinol bases of crystal-violet and malachite-green in ethyl alcohol, ether, benzene, and chloroform have been exposed to the action of light from a quartz mercury lamp and the colour changes noted. In all cases, except that of the leuco-cyanide of victoria-blue, the originally colourless or at most faintly coloured solution became intensely coloured. In the case of victoria-blue, the solution showed no colour change until a temperature of 35—40° had been reached, and then the change was very slight; at 78°, the reaction reached its optimum

value. The reactions in all cases took place more slowly in ether and benzene than in alcohol. The reaction in the dark was very slow, but it was strongly catalysed by the presence of potassium hydroxide or potassium cyanide. It is shown that the reaction is reversible in all cases and consequently is to be regarded as an energy-storing reaction. The specific conductivity of some of the solutions has been determined at various periods after preparation, and in this way the stationary condition has been determined both for the light and the dark reactions. It is shown that the active portion of the light is that composing the long wave-length portion of the ultra-violet. The dark reactions are readily catalysed and the formation of molecular compounds plays an important part in the catalysed reaction. Photo-concentration cells of the type Electrode (2nd kind)|Solution (dark)||Solution (bright)|Electrode (2nd kind) have been measured. It is shown that considerable *E.M.F.* values may be obtained. Thus the cell Ag,AgCN|*p*-rosaniline leuco-cyanide (dark)||*p*-rosaniline leuco-cyanide (light)|AgCN,Ag gave an *E.M.F.* of 0·213 volt, whilst the leuco-cyanide of malachite-green gave the value 0·224 volt. The *E.M.F.* values became steady in a few minutes after the illumination commenced. In the case of the carbinol base, the electrode Ag,Ag_2O| was used, and in these cases a very small *E.M.F.* was obtained. J. F. S.

The Existence of Helium Nuclei in the Nuclei of Radioactive Elements. F. BRÖSSLERA (*Rev. Chim.*, 1921, **1**, 42—48, 74—80).—The mass of a helium nucleus is less than that of the four hydrogen nuclei, from which it may be supposed to be formed, by an amount $\Delta m=4\times1{\cdot}0077-4{\cdot}002=0{\cdot}029$. This corresponds with a loss of energy during the condensation of the hydrogen nuclei of $0{\cdot}029c^2$ per gram-atom of helium formed (c=velocity of light). Consequently, it is unnecessary to suppose that helium nuclei pre-exist in the nuclei of radioactive elements in order to account for the kinetic energy possessed by α-particles, for part of the energy liberated during the formation of helium nuclei within the atom from pre-existing hydrogen nuclei might be utilised in detaching the α-particles so formed and imparting to them their momentum. C. K. I.

The Degradation of Gamma-Ray Activity. ARTHUR H. COMPTON (*Phil. Mag.*, 1921, [vi], **41**, 749—769).—The greater part of the secondary γ-radiation from matter traversed by hard γ-rays from radium *C* is fluorescent in character. It is harder and more intense at small angles with the incident beam. At large angles, the radiation from heavy elements is somewhat more penetrating than that from light elements, but at small angles the hardness and intensity are approximately the same from elements covering a wide range of atomic numbers. The wave-length of the softest parts of the radiation lies between 0·06 and 0·12 Å.U., probably nearer the former value, whilst the wave-length of the hardest part is probably about half as great. The effective wave-length of the hard γ-rays from radium is estimated as about 2 or 3×10^{-10} cm.

J. R. P.

The Absorption of *X*-Rays. TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1920, **4**, No. 3, 1—44).—The relative absorption coefficients for *X*-rays of a number of elements have been determined by a method previously described (A., 1917, ii, 350). The law of additive absorption was confirmed. With the possible exception of carbon, the state of aggregation appears to have no influence on the quantity of absorption. In compounds containing an element with different valencies, no difference in the absorptions was found. The relation between the atomic absorption coefficients for most elements from hydrogen to barium, and lead, with the absorption coefficient of copper as standard, have been determined at the mean wave-lengths 0·38, 0·36, 0·34, and 0·30 (10^{-8} cm.). On the assumption that the absorption with hydrogen is exclusively due to scattering produced by the one electron associated with the nucleus, the conclusion is drawn that the effect with other elements is due to the outer electrons, and the number of these was calculated as follows: hydrogen 1, lithium 3, glucinum 4, boron 5, carbon 4, nitrogen 7, oxygen 4, fluorine 5, sodium 7, magnesium 4, aluminium 5, silicon 4, phosphorus 7, sulphur 4, chlorine 5, potassium 7, calcium 4. The atomic absorption coefficient increases almost in proportion to the atomic number. The number of outer electrons in the lightest elements seems to be the same for elements in the same vertical row in the periodic system. J. R. P.

Scattering and Absorption of Hard *X*-Rays in the Lightest Elements. TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1920, **4**, No. 5, 1—12; *Phil. Mag.*, 1921, [vi], **41**, 733—743).—The atomic absorption coefficients of carbon, hydrogen, nitrogen, and oxygen relative to the molecular absorption coefficient of water were determined. The results did not agree with the theories of Thomson, according to which the scattering effect is independent of wave-length, or of Schott, according to which the mass-scattering coefficient should approach a constant value. The results were in agreement with the theory of Compton (A., 1919, ii, 504). In the case of lighter elements as far as and including nitrogen, the absorption can be considered chiefly as a scattering effect, the true absorption being very small. True absorption is proportionally greater with oxygen than with lighter elements, which is taken to indicate that the outer electrons are four in number in that element.

J. R. P.

Action of Röntgen Rays on Chloroform Solutions of Iodoform. L. BAUMEISTER and R. GLOCKER (*Zeitsch. physikal. Chem.*, 1921, **97**, 368—375).—The authors have studied the action of Röntgen rays on a 2% solution of iodoform in chloroform with the object of ascertaining whether or no the amount of iodine liberated constitutes a measure of the intensity of the radiation. The experiments show that the amount of iodine liberated in no way represents the energy of radiation, as has been hitherto assumed. The action of the Röntgen rays is not to liberate iodine, but rather to loosen it; the major portion of the iodine liberated is due to a

secondary reaction which has a velocity that is entirely independent of the quality and quantity of the radiation. Consequently this reaction may not be used as a measure of the energy of the radiation.

J. F. S.

Radiating and Ionisation Potentials of Hydrogen. K. T. COMPTON and P. S. OLMSTEAD (*Physical Rev.*, 1921, **17**, 45—53).—To detect and distinguish between radiation and ionisation, a modification of Lenard's method was used. Both radiation and ionisation are obtained at about 10·8 volts, probable radiation at about 13·4 volts, and strong ionisation at 15·9 volts. Discrepancies in experimental results are ascribed to the possibility of the following effects occurring together: radiation from free atoms near 10·8 volts, and ionisation near 13·5 volts; ionisation without dissociation of molecules near 10·8 volts, dissociation with radiation from one of the atoms near 13·4 volts, and dissociation with ionisation of one atom near 15·9 volts.

CHEMICAL ABSTRACTS.

Ionisation and Resonance Potentials of some Non-metallic Elements. F. L. MOHLER and PAUL D. FOOTE (*U.S. Bureau of Standards, Sci. Papers*, 1920, No. **400**, 669—700. Compare this vol., ii, 8; also A., 1918, ii, 94; A., 1919, ii, 42; A., 1920, ii, 464 and 524).—The following values have been obtained for ionisation potentials (V_i) and resonance potentials (V_r):—For phosphorus, $V_r = 5{\cdot}80 \pm 0{\cdot}1$ volts; $V_i = 13{\cdot}3 \pm 0{\cdot}5$ volts. For iodine, $V_r = 2{\cdot}34 \pm 0{\cdot}2$ volts; $V_i = 10{\cdot}1 \pm 0{\cdot}5$ volts. For sulphur, $V_r = 4{\cdot}78 \pm 0{\cdot}5$ volts; $V_i = 12{\cdot}2 \pm 0{\cdot}5$ volts. For nitrogen, $V_r = 8{\cdot}18 \pm 0{\cdot}1$ volts; $V_i = 8{\cdot}7 + 8{\cdot}18 = 16{\cdot}9 \pm 0{\cdot}5$ volts. For oxygen, $V_r = 7{\cdot}91 \pm 0{\cdot}5$ volts; $V_i = 7{\cdot}9 + 7{\cdot}6 = 15{\cdot}5 \pm 0{\cdot}5$ volts. For hydrogen, First $V_r = 10{\cdot}4 \pm 0{\cdot}5$ volts; First $V_i = 13{\cdot}3 \pm 0{\cdot}5$ volts; Second $V_r =$ about 12·2 volts; Second $V_i = 16{\cdot}51 \pm 0{\cdot}5$ volts. Bohr's theory gives, for the hydrogen atom, $V_r = 10{\cdot}16$ and $V_i = 13{\cdot}54$; for the hydrogen molecule, $V_i = 16{\cdot}26$. The difference between these ionisation potentials is therefore as follows: observed, $3{\cdot}24 \pm 0{\cdot}5$ volts; calculated by Bohr, 2·72 volts; calculated from Langmuir's heat of dissociation (A., 1914, ii, 104), 3·90 volts. There is no evidence that any of the ionisation potentials measured are "negative ionisation potentials" required to remove an electron from a negatively charged ion to form a neutral molecule.

CHEMICAL ABSTRACTS.

Ionisation of Gases during Chemical Reactions. II. A. PINKUS and M. DE SCHULTHESS (*J. Chim. phys.*, 1920, **18**, 366—411; *Helv. Chim. Acta*, 1921, **4**, 288—295. Compare A., 1918, ii, 286).—Making use of the method previously described, the authors have ascertained the amount of ionisation which occurs when certain gaseous reactions are allowed to take place at the ordinary temperature. The reactions studied are, the formation of nitrosyl chloride from chlorine and nitric oxide, the decomposition of ozone, and the reaction between ozone and nitric oxide and nitrogen dioxide respectively. In the case of the combination of chlorine and nitric oxide, it is shown that at ordinary temperatures bi-polar nucleii are emitted, the emission being entirely due to the chemical reaction itself, and not in any way influenced by any physical process.

Generally, the ionisation is very intense, but the number of charged particles received by the electrode is always very much less than the number of nitrosyl chloride molecules formed. This is explained, at least in part, by the recombination of the ions before they reach the electrode. The ionisation is favoured by an excess of chlorine, the strongest effect being observed when 1 to 4 volumes of chlorine are mixed with one volume of nitric oxide. The number of charges received by the electrode in a given time is independent of the pressure of the reacting mixture. The ionisation persists generally for a few minutes only, and its intensity decreases much more rapidly than the rate of formation of the nitrosyl chloride. The results generally indicate that the ionisation is brought about by the reaction of at least one molecule of chlorine with one molecule of nitric oxide and it occurs more rapidly than the reaction $2NO+Cl_2=2NOCl$. The decomposition of ozone at ordinary temperatures is accompanied by a bi-polar ionisation which is probably to be attributed to the decomposition itself. The ionisation in this case is very intensive, particularly when the reaction occurs in the presence of a large excess of chlorine. As in the preceding case, the number of charged particles received by the electrode is much less than the number of molecules which have reacted. In the presence of chlorine, the intensity of ionisation becomes greater as the volume ratio $Cl_2 : O_3$ is increased. The action of chlorine in the reaction is a purely catalytic one. The ionisation diminishes somewhat with an increase in the pressure of the reacting mixture, and it persists from one to three minutes in the presence of a large excess of chlorine, whilst in pure ozone or ozone slightly diluted with chlorine it is much less persistent. The ionisation diminishes more rapidly as the reaction causing it is more rapid. The reactions between concentrated ozone and nitric oxide or nitrogen dioxide take place with the evolution of light and very often partake of the character of an explosion, even when the quantity of ozone present is very small. In the case of the reaction with nitrogen dioxide, a very strong bi-polar ionisation accompanies the reaction, which appears to be due entirely to the reaction itself, but this is not quite certain, because the product of the reaction, nitrogen pentoxide, is solid and because of the violence with which the reaction takes place. J. F. S.

Ionisation of Gases during Chemical Reactions. III. A. PINKUS (*J. Chim. phys.*, 1920, **18**, 412—413. Compare preceding abstract).—The author points out that the reason for the failure of Trautz and Henglein (A., 1920, ii, 346) to observe ionisation during the combination of chlorine and nitric oxide is that their experimental procedure is unfavourable to easy measurement of the change. J. F. S.

Disappearance of Gas in the Electric Discharge. II. THE RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LTD., LONDON (*Phil. Mag.*, 1921, [vi], **41**, 685—706; see A., 1920, ii, 730).—In the presence of incandescent tungsten, hydrogen disappears without the passage of the discharge, the gas adhering with-

out change to the surface of the glass, especially to the cooler parts. When the discharge passes, the rate of disappearance of hydrogen is not greatly altered, but there is simultaneous liberation of adsorbed gas by bombardment and appearance of water vapour. Carbon monoxide is converted in the discharge into dioxide, both gases adhering to the glass walls, from which they can be liberated by heating. Nitrogen disappears under discharge, but cannot be liberated again by baking the vessel; at the same time, the filament wastes and the walls are blackened. Langmuir's nitride, WN_2, is probably formed, but part of the gas may be held to the walls by a covering layer of tungsten. Argon disappears with much blackening of the bulb, but may be liberated by baking together with hydrogen produced by bombardment of the glass. Mercury has not been proved to disappear; the discharge through the vapour liberates large quantities of gas from the glass, even after previous baking in a high vacuum. Phosphorus vapour rapidly disappears and is converted into red phosphorus deposited on the walls. The glow potential of phosphorus vapour is anomalous. Hydrogen, carbon monoxide, and nitrogen mixed with phosphorus vapour disappear with the phosphorus; a lower final pressure of gas may be attained with a given applied potential in the presence of phosphorus. Chemical action of the phosphorus is not considered probable; the deposited red phosphorus may cover the deposited gas and prevent its liberation by bombardment; at the same time, it provides a new surface for adsorption. J. R. P.

Solutions of Metals in Non-metallic Solvents. VI. The Conductivity of the Alkali Metals in Liquid Ammonia. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1921, **43**, 749—770. Compare A., 1907, ii, 935; 1908, ii, 486, 834, 835; 1914, ii, 520).—The conductivity of solutions of sodium, potassium, lithium, and mixtures of sodium and potassium in liquid ammonia at the boiling point of liquid ammonia have been determined. From a consideration of the results of the present work and that previously published (*loc. cit.*), it is shown that an ionic equilibrium exists in solutions of a metal in liquid ammonia, and that the negative carrier is identical for all metals, and exhibits abnormal conducting power in the case of the more concentrated solutions. It follows as a consequence that the conductivity curve for such solutions should exhibit a minimum. In keeping with experimental fact, it is shown that the conductivity curve for dilute solutions should correspond approximately with that of ordinary salts in liquid ammonia. In the more concentrated solutions, the conductivity curve should rise with increasing concentration owing to the increase in speed of the negative carrier. The conductivity curves of sodium, potassium, and lithium, as well as those of mixtures of sodium and potassium, are similar in form, but are displaced as regards the value of the conductivity. The difference in the conductivity of the more dilute solutions corresponds approximately with the difference in the conductivity of the positive ions of these metals. Solutions of metals in liquid ammonia appear to form the connecting link between metallic and electrolytic conductors. It has been definitely shown that the conduction process

is an ionic one and there is nothing to distinguish the more concentrated solutions from actual metallic substances. It may therefore be concluded that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, it may be concluded that it is identical with the negative electron as it appears in radioactive and other phenomena.

J. F. S.

Abnormality of Strong Electrolytes. DAVID LEONARD CHAPMAN and HERBERT JOHN GEORGE (*Phil. Mag.*, 1921, [vi], **41**, 799—801).—In the calculations of Ghosh (T., 1918, **113**, 449, 627, 707, and 790), the number of ions having kinetic energies in excess of a given value has been obtained by an incorrect formula. When the correct expression is used the results are no longer in good agreement with experiment. J. R. P.

Electrical Properties and Peptisation of Colloids. GEORG VARGA (*Koll. Chem. Beihefte*, 1919, **11**, 3—33).—The electrical conductivity of stannic acid suspensions has been determined at 25° for a series of concentrations by shaking a definite quantity of stannic acid with potassium hydroxide and measuring the conductivity, then allowing the suspension to settle, and again determining the conductivity, the difference between the two values giving the conductivity of the suspension. The hydrogen-ion concentration of stannic acid suspensions has been determined by the indicator method in a Coehn apparatus as modified by Galecki (A., 1912, ii, 263). Conductivity values and hydrogen-ion concentrations were also made in suspensions which had been boiled for considerable periods. The migration of stannic acid suspensions has also been determined. It is shown theoretically that the quantity of electricity transported by the stannic acid particles may be calculated by the formula $E_{SnO_2}=K_m/K_s \times E_s . U_{SnO_2}/(U_k+U_{SnO_2})$ in which K_m is the conductivity of the micellæ, K_s that of the suspension or sol, U_k and U_{SnO_2} the velocities of the potassium and stannate ions respectively in cm./sec. under a potential drop of 1 volt/cm., and E_s and E_{SnO_2} the quantities of electricity carried by the suspension and the stannate ion respectively. The author develops a theory of peptisation, and a theoretical introduction to the paper is added by R. Zsigmondy. J. F. S.

The Electromotive Behaviour of Aluminium. II. A. SMITS and G. J. DE GRUIJTER (*Proc. K. Acad. Wetensch. Amsterdam*, 1921, **23**, 966—968. Compare A., 1920, ii, 579).—With the object of obtaining a clearer insight into the electromotive behaviour of aluminium and its alloys with mercury, the melting point composition diagram has been constructed, from which it is shown that no intermetallic compounds are formed between these metals. It is shown that, assuming Gibbs's paradox is applicable to the components of a mixed crystal phase present in dilute solution, the formula $E=-0{\cdot}058/vF.\log L_M/M_L^v-2{\cdot}8$ represents the experimental potential. It is to be expected that the potential of

aluminium in a solution of aluminium ions should become less negative by the addition of a little mercury, but the reverse is found to be the case, and this to a considerable degree. This indicates that mercury dissolved in aluminium is a catalyst for the internal transformations of aluminium. J. F. S.

The Current Produced when a Soldered Junction is Submitted to Pressure. M. POLÁNYI (*Zeitsch. physikal. Chem.*, 1921, **97**, 459—463).—A theoretical paper in which it is shown that if a conducting circuit is made of two pieces of different metal wires soldered together at each end, and one junction is submitted to a pressure, an *E.M.F.* will be set up. This conclusion is based on the assumption that material particles always travel with an electric current. It is shown that this *E.M.F.* may be readily determined in certain cases, and it will have a value of several centi-volts for moderate pressures. A measurement of this effect will naturally lead to a knowledge of the transport numbers of solid electrolytes and also to the ratio of the electronic conductivity to the material conductivity in poor conductors of electricity. J. F. S.

The Alleged Uselessness of the Weston Normal Element. W. JAEGER and H. VON STEINWEHR (*Zeitsch. physikal. Chem.*, 1921, **97**, 319—329).—An answer to Cohen and Moesveld's assertion that the Weston element is metastable even at ordinary temperatures (A., 1920, ii, 581). It is shown that the Weston element containing 12·5% amalgam behaves exactly in the same way as the previously used element containing 14·3% amalgam, and that at ordinary temperatures both are absolutely normal in their behaviour. At temperatures below the transition point of 12·1° given by Cohen and Moesveld for the 12·5% amalgam, not a single element, out of sixty examined at the Reichsanstalt, exhibited any divergence. The divergence of the *E.M.F.* observed by Smith (*loc. cit.*) at 0° was due to the use of an amalgam which had been suddenly cooled in its preparation, and elements prepared with this material become quite normal immediately at ordinary temperatures. It is shown that the measurements on which Cohen and Moesveld base their assertion are not permissible, because the elements concerned were already above the "branching point" and had not been cooled below it, but nevertheless they exhibited values which were markedly divergent from the normal value. J. F. S.

The Hydrogenation of Quinhydrones. EINAR BIILMANN (*Ann. Chim.*, 1921, [ix], **15**, 109—157).—It is possible to prepare with aqueous solutions of quinhydrones reversible electrodes with very constant potential. Such electrodes may be used to determine hydrogen-ion concentration in a number of cases where the use of an ordinary hydrogen electrode is not possible. Such electrodes have been constructed with *p*-benzoquinone, toluquinone, and xyloquinone. The potentials of hydrogenation found in the three cases are, for *p*-benzoquinone 0·7044 volt at 18° and 0·6990 volt at 25°; for toluquinone 0·6507 volt at 18° and 0·6454 volt at 25°; and for

xyloquinone 0·6014 volt at 18° and 0·5960 volt at 25°. Thus the value $\pi_{18}-\pi_{25}$ is the same in each case, and, further, the variation in the potential due to the introduction of the first methyl group is less than that due to the introduction of the second methyl group. The heats of hydrogenation of the three quinones calculated from the hydrogenation potentials are, for *p*-benzoquinone U=42·8 cal.; for toluquinone U=40·1 cal., and for xyloquinone U=38·1 cal.

An electrode prepared from benzoquinone was found to be more convenient and rapid in rise than a hydrogen electrode in measuring the hydrogen-ion concentration of such solutions as those of the mineral acids. In addition, it could be used for such measurements with solutions of compounds containing ethylenic and acetylenic linkings such as solutions of acrylic, crotonic, fumaric, maleic, and phenylpropiolic acids; also with halogenated acids such as chloroacetic acid, and with an amino-acid of the type of glycine.

W. G.

The Measurement of Electrolytic Resistance Using Alternating Currents. H. F. HAWORTH (*Trans. Faraday Soc.*, 1921, **16**, 365—391).—When an alternating current is sent through a solution, and the electrical constants of the apparatus between the electrodes are determined, the cell appears as a capacity in series with a resistance. A special apparatus of the bridge type was designed for measuring the capacity and resistance of cells at constant temperature (±0·001°), and experiments were made to determine the variation of apparent resistance and capacity with the frequency *f* of the alternating current, using both plain and platinised platinum electrodes. Experiments with potassium chloride cells, using non-platinised electrodes, showed that the apparent resistance diminished with increasing frequency; with 0·1*N*-KCl the resistance $R=22{\cdot}24f^{-0{\cdot}20}$ at 25°, whilst with 0·025*N*-KCl, $R=42{\cdot}96f^{-0{\cdot}109}$. When platinised electrodes were used, the variation of resistance with frequency was much less, but the capacity of the cell was increased enormously. Comparative dilution experiments with both platinised and unplatinised electrodes showed that, in the former case, as the dilution increased the effect of variation of frequency became more pronounced, whereas with plain electrodes it diminished, until at high dilutions there is little to choose between the two forms of electrode. The effective capacity of the cell decreases with increasing dilution. A graphic method was devised by which, from observations of the apparent resistance at two different frequencies, using unplatinised electrodes, the true resistance of the cell can be found by extrapolating to infinite frequency. The value thus found agreed very nearly with the value obtained experimentally, using platinised electrodes at the same dilution, in the cases of potassium chloride, sodium, ferric, nickel, and cobalt chlorides, but with ammonium chloride the agreement was not so good.

The effect of platinising the electrodes is not considered to be due to an increase in area, but more probably to absorption of the normal gas film, which behaves as a leaky condenser, by the

"spongy" platinum, thus enormously increasing the capacity of the electrodes to the electrolyte, reducing the voltage across this dielectric per unit current and reducing the losses. Experiments using strong solutions and low resistance cells have shown, by various potentiometer measurements, that the resistance of an electrolyte is independent of the frequency, provided that the potential electrodes are put into an electrical backwater, that is, out of the main current stream. E. H. R.

Electrolysis of Water and a Oxy-hydrogen Gas Element. EMIL BAUR (*Helv. Chim. Acta*, 1921, **4**, 325—333).—With the object of storing seasonal water-power, the author has devised an apparatus by means of which fused aqueous sodium hydroxide is electrolysed, sheet-iron electrodes being employed. Only the hydrogen generated is stored and is used subsequently in conjunction with air in an element in which electric current is produced by the union of the hydrogen and oxygen in contact with fused sodium hydroxide, electrodes in the form of iron grids being used. T. H. P.

The Electrolysis of Solutions of Sodium Nitrite, using a Copper Anode. F. H. JEFFERY (*Trans. Faraday Soc.*, 1921, **16**, 453—457).—The electrolysis of solutions containing 6·9, 13·8, and 27·6 grams of sodium nitrite per 100 c.c. was studied, using a current of 0·16 ampere, with a copper anode, the arrangements of the electrolysis vessel being similar to those in the experiments with a silver anode (A., 1920, ii, 662). The copper went into solution, forming a dark yellowish-green anolyte, whilst a bluish-green solid was formed on the anode and some gas was evolved from this electrode. No copper was deposited on the cathode. The copper complex in the anolyte contained bivalent copper, since sodium hydroxide gave an immediate precipitate of cupric hydroxide, whilst ammonium thiocyanate gave no precipitate. By addition of potassium and lead nitrate to the anolyte and allowing to crystallise, well-formed black crystals of the compound $K_2Pb[Cu(NO_2)_6]$ were obtained, and from these, by means of potassium sulphate, dark olive-green crystals of $K_4[Cu(NO_2)_6]$ were prepared. These are regarded as salts of cupri-nitrous acid, $H_4[Cu(NO_2)_6]$. The gas evolved from the anode was pure nitric oxide. The solid deposited on the anode had the same composition, however the concentration of sodium nitrite was varied, and corresponded with the formula $Cu(NO_2)_2,CuO$. It is slowly hydrolysed by water. When the electrolysing current was increased to 0·35 ampere, copper was slowly deposited on the cathode at all concentrations of sodium nitrite. E. H. R.

Thermal Expansion of Liquids. W. HERZ (*Zeitsch. physikal. Chem.*, 1921, **97**, 376—381).—A theoretical paper in which the author has examined the nature of the constant a, contained in the formula, $V_0/V_t=(a\theta-T)/(a\theta-273)$, put forward by Thorpe and Rücker (T., 1884, **45**, 135) to represent the dependence of specific volume of liquids on the temperature. It is shown, by considering a large number of cases, that this formula represents the facts only to a

restricted degree. The constant a is in reality not constant, since it decreases with increasing temperature. In most series of analogous substances, a increases with the molecular or atomic weights respectively. With the exception of water, the value of a lies in all cases between 1·5 and 2·1. Water is exceptional, because of its anomalous density. The constant a enters into an equation representing the thermal expansion of liquids put forward by Oswald (A., 1912, ii, 230) and Davies (A., 1912, ii, 426) which has the form $\alpha=1/(a\theta-T)$. Here the coefficient of expansion can be calculated from the critical temperature. The coefficient of expansion is smaller the higher the critical temperature. J. F. S.

Specific Heat of Aqueous Salt Solutions. KARL JAUCH (*Zeitsch. Physik*, 1921, **4**, 441—447).—The specific heats of aqueous solutions of chloric and iodic acids, the chlorides of lithium, barium, aluminium, thorium, and mercury, the bromides of lithium, sodium, magnesium, cæsium, indium, and rubidium, the iodides of lithium and sodium, the fluorides of potassium and thallium, the nitrates of glucinum, aluminium, lanthanum, samarium, cæsium, and lead, and lithium chlorate and iodate have been determined at 18° in various concentrations generally lying between $0{\cdot}5M$ and $5{\cdot}0M$. The results are discussed in connexion with the specific volume and the ionisation. J. F. S.

Equation of Condition for Liquids. K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1921, **97**, 445—458).—A mathematical paper in which from the general form of the equations of condition for liquids, $p=p_k-p_a=fRT/v-a/v^u$, the author develops for monatomic substances the equation $p=p_k-p_a=fRT/v-p_a=kv^{1/3}/(v^{1/3}-b^{1/3})\times RT/v-a/v^{2\cdot5}$. This equation is applied particularly to the case of mercury and various physical constants evaluated from known data. These include the coefficient of compressibility, $1{\cdot}336\times10^{-6}$, the coefficient of expansion, $1{\cdot}807\times10^{-4}$, both values for 0°; at 400° the values become $5{\cdot}803\times10^{-6}$ and $1{\cdot}835\times10^{-4}$ respectively. A number of calculations are made for ethyl ether. J. F. S.

Thermodynamics of Mixtures. VI, VII, and VIII. MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1921, **97**, 330—336, 337—342, 343—367. Compare this vol., ii, 162, 180, 301).—A series of mathematical papers in which the thermodynamic treatment of mixtures is further developed. In the present papers, the author develops a thermodynamical theory of mixtures, of any concentrations, in which no use is made of the Nernst theorem or of the hypotheses of Planck. The absolute entropy of mixtures is treated in the second paper, and the third paper deals with the conditions of reversibility, especially in the case of two component two phase purely physical systems. J. F. S.

Freezing Points of Binary Aqueous Solutions of Electrolytes. OSKAR KLEIN and OLOF SVANBERG (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1920, **4**, No. 1, 1—13).—The freezing points of solutions containing two salts were determined by Dernby's method

(*ibid.*, 1916, **3**, No. 18). No general law expressing the sign of the neutral salt action was found. In some cases the lowering of freezing point is smaller, in others greater, than the sum of the individual depressions. The salt action is positive with most electrolytes, with sulphates, nitrates, and alkali hydroxides the action is negative. The value of $K=\delta/c_1c_2$, where δ is the difference between the lowering for the solution and the calculated sum of the individual lowerings, c_1 and c_2, are the concentrations of the two salts, is used to express the salt action. In mixtures of halogen hydracids and haloids of alkali-metals K is positive and fairly constant. With salts of alkaline-earths, K is also positive but increases with concentration. J. R. P.

The Three-Temperature Rule. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1920, **18**, 359—361; *Ann. Chim.*, 1921, [ix], **15**, 212—220).—In previous papers (this vol., ii, 83, 84), the author has shown that $T_f(T_c-T_f)|T_1(T_c-T_1)=r$ and $T_c|(T_1+T_f)=r'$, in which T_c T_1 and T_f are respectively the absolute values of the critical, normal boiling, and freezing temperatures, and r and r' constants. Generally r and r' are very nearly equal. In certain cases, these two values are identical to the second place of decimals; this occurs with water, phosphine, arsenic trichloride, methyl bromide, methyl iodide, *m*-xylene, 1:3:5-trimethylbenzene, chloro-, bromo-, and iodo-benzene, titanium tetrachloride, and acetonitrile. For these cases, the two equations may be equated, and the expression $T_f(T_c-T_f)/T_1(T_c-T_1)=(T_1+T_f)/T_c$ obtained. This is developed into a cubic equation in T_1 of the form $T_1^3-(T_c-T_f)T_1^2-T_cT_fT_1+T_cT_f(T_c-T_f)=0$ which has the roots (T_c-T_f), $\sqrt{T_cT_f}$, and $-\sqrt{T_cT_f}$. It is shown that the observed value of T_1 only agrees with the root T_c-T_f when both sides of the identity above have the value unity. And the author deduces that for each substance there is a vapour tension at which $T_c=T_1+T_f$. J. F. S.

Some New Methods for the Determination of the Vapour Pressure of Salt Hydrates. ROBERT E. WILSON (*J. Amer. Chem. Soc.*, 1921, **43**, 704—725).—The methods used by previous investigators in the determination of the vapour pressure of salt hydrates are described in fair detail and their defects pointed out. The author advances reasons for choosing a new type of indirect method for determination of this quantity. The method consists in the establishment of equilibrium between the hydrates and a solution of water in *iso*amyl alcohol, followed by an estimation of the water content of the resulting mixture. Three new quantitative methods are described for estimating the water content of *iso*amyl alcohol solutions, (*a*) colorimetric comparison of standard cobalt chloride solutions; (*b*) determination of the conductivity of standard cobalt chloride solutions; (*c*) determination of the conductivity of saturated potassium thiocyanate solutions. The last-named method is the one preferred. Data are given on the colour and conductivity of cobalt chloride solutions in amyl alcohol as a function of the temperature and water content; approximate values are also given for the conductivity of a large number of other salts in

anhydrous and aqueous amyl alcohol. The solubility of water in *iso*amyl alcohol is found to be 9·77% at 25°. To establish the vapour pressure–water content curve for *iso*amyl alcohol solutions, it was necessary to determine with great accuracy the pressure of aqueous vapour of a few hydrated salts. This has been done for the pairs $CuSO_4,5H_2O \longrightarrow 3H_2O$; $BaCl_2,2H_2O \longrightarrow H_2O$; $Na_2HPO_4,12H_2O \longrightarrow 7H_2O$; $Na_2HAsO_4,7H_2O \longrightarrow 2H_2O$ and $Na_2SO_4,10H_2O \longrightarrow Na_2SO_4$, all at 25°. The method adopted consisted in placing the salts in a small balance inside a desiccator fitted with a fan and stirrer and containing sulphuric acid solution, the strength of which was varied until the concentration was found at which the salt neither gained nor lost weight. This method is found to be very satisfactory for salts which gain or lose water with fair rapidity. J. F. S.

Determination of the Vapour Pressure of Salt Hydrate by a Distribution-Conductivity Method. ARTHUR A. NOYES and LEON R. WESTBROOK (*J. Amer. Chem. Soc.*, 1921, **43**, 726—734. Compare Wilson, preceding abstract).—A detailed description of Wilson's distribution method for the determination of the vapour pressure of salt hydrates. The method consists in shaking the salt hydrate with anhydrous *iso*amyl alcohol, or *iso*amyl alcohol containing a known small quantity of water until equilibrium is set up and then analysing the alcoholic phase to determine its water content by saturating it with solid potassium thiocyanate and measuring the electrical conductivity of the mixture. The development of the method into a practically useful form involved the determination of the electrical conductivity of *iso*amyl alcohol solutions of known water content saturated with potassium thiocyanate and the determination of the water content in *iso*amyl alcohol solutions which had been brought into equilibrium with pairs of hydrates of accurately known vapour pressure. The conductivity of water–*iso*amyl alcohol mixtures saturated with potassium thiocyanate has been determined at 25° for water percentages between 0 and 3·016. The solubility of water in *iso*amyl alcohol is found to be 9·884% at 25°. This value is about 1% higher than that found by Wilson (*loc. cit.*), but since the vapour pressure–water content curve is very flat in this vicinity the difference between the two values is of little moment. A vapour pressure–composition diagram for water–*iso*amyl alcohol mixtures is constructed, which is probably typical for liquids of limited but considerable miscibility. J. F. S.

The Vapour Pressures of Mixtures. ALFRED W. PORTER (*Trans. Faraday Society*, 1921, **16**, 336—345).—The fundamental relation between the vapour pressures of the constituents of a binary liquid mixture and the composition of the mixture is given by Duhem's differential equation

$$\mu_a \cdot (\partial \log \Pi_a)/(\partial \mu_a) = \mu_b (\partial \log \Pi_b)/(\partial \mu_b)$$

where μ_a and μ_b are the molar fractions of the components and Π_a and Π_b are the respective vapour pressures. A new thermodynamic proof of this theorem is given, assuming that the vapour mixture follows the perfect gas law, that is, that the partial pres-

sures of the components are additive. This equation was integrated by Margules, from whose solution it can be shown that $\pi_a = \Pi_a \mu_a e^{\beta(1-\mu_a)^2}$, where Π_a is the value of π_a when μ_a becomes unity. Similarly, $\pi_b = \Pi_b(1-\mu_a)e^{\beta\mu_a^2}$. The experimental results of Sameshima on the vapour pressures of mixtures of acetone and ethyl ether (A., 1918, ii, 429) agree very well with the figures calculated from these equations. The value of the constant β for these mixtures is 0·7414, and it increases slightly as the temperature is lowered. A diagram is given showing the different kinds of curve obtained, when relative vapour pressure is plotted against molar concentration in the liquid mixture, from the equation $\pi_a/\Pi_a = \mu_a e^{\beta(1-\mu_a)^2}$ for different values of β from +3 to −3. When β=0 the partial pressure curve is a straight line; for positive values of β it lies wholly above this line, and for negative values wholly below it. For β=2 there is a horizontal point of inflexion and for higher values there are two points, on either side of a maximum, for which the vapour pressure is the same. This is of importance in connexion with the equilibrium of partly miscible liquids. For mixtures of methyl alcohol and glycerol β=1; for acetone and oleic acid about 0·5; for ether and oleic acid −0·2. In the case of sulphuric acid–ethyl ether mixtures, an abnormal curve is obtained; for the lower part of the curve β=−6, but when the proportion of ether in the mixture becomes large the curve requires a positive value of β. In such cases as this, and only in such cases, it appears necessary to introduce a chemical hypothesis to explain the phenomena.

In the second part of the paper it is shown mathematically that the Duhem–Margules equations can be extended to systems of higher order than the binary. E. H. R.

Vapour Tension and Molecular Volume of Toluene–Benzene Mixtures. ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1921, **97**, 417—425).—In a previous paper (A., 1919, ii, 390) the author describes a number of determinations of the vapour tension of mixtures of toluene and benzene. These results are now examined together with further data published for the first time in the present paper. The vapour tension curves of the mixtures at ordinary temperatures are concave toward the concentration axis, but at 60° become straight lines and remain so at 79·7° and 120·3°. The vapour tension isothermal shows that at ordinary temperatures toluene is fairly strongly associated, and this is in keeping with the volume change which occurs when the mixtures are prepared. An hypothesis of the volume dilation is developed on the basis of the theory of concentrated solutions and with the assumption that one component is bimolecular. The volume dilation curve has been constructed from calculations based on the molecular constitution of the mixtures and found to be in excellent agreement with the experimental curve. This indicates that the conclusions drawn from the vapour tension isothermal are in keeping with those drawn from other physical properties, and consequently furnishes a confirmation of the theory of concentrated solutions.

J. F. S.

Principles of New Methods Applicable to the Determination of Molecular Weights. CAMILLE MATIGNON (*Compt. rend.*, 1921, **172**, 1036—1038).—If in a system $A_{\text{liq.}} \rightleftharpoons B_{\text{gas}}+C_{\text{sol}}$, where C is insoluble in A, a weight π of a substance, having a molecular weight M and without physical or chemical action on B or C, is dissolved in 100 grams of A, then if the vapour tension of B, represented by p_b, is thereby diminished by an amount x,

$$x=Kp_b\pi/p_aM,$$

where K is a constant depending only on the nature of A. This principle is further developed for a bivariant system. W. G.

The Use of Enamelled Bombs in Calorimetry. C. MATIGNON and (MLLE) G. MARCHAL (*Compt. rend.*, 1921, **172**, 921—922).—Two instances are quoted where two enamelled calorimetric bombs of the Mahler type and of recent manufacture were attacked by the nitric acid, such as is always formed in the ordinary conditions of calorimetric work. To obviate this source of error, new bombs should be filled with N-nitric acid and submitted to its action for four or five hours before being used. W. G.

Modifications of the Adiabatic Calorimeter. W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1921, **43**, 875—876).—The author describes modifications of his adiabatic calorimeter (A., 1915, ii, 420), whereby the temperature of the jacket can be brought to 0·1° of that of the calorimeter in one and a half minutes after the reaction starts, and to within a few thousandths of a degree in five minutes. The heating and cooling of the jacket are effected by hot or cold water introduced from without by means of a current of air. J. F. S.

Heat of Combustion of Benzoic Acid, Naphthalene, and Sucrose. F. HENNING (*Zeitsch. physikal. Chem.*, 1921, **97**, 467—477).—A critical consideration of the data appearing in the literature on the heat of combustion of sucrose, benzoic acid, and naphthalene. It is shown that data put forward do not allow of any conclusions being drawn as to which of the above-named substances is most suited for normal determinations. The absolute values of the heat of combustion, determined by the different observers, fluctuate as much as 2·5% from the mean value. The ratio of the heats of combustion of these substances varies 2—3%, which indicates, probably, impure materials in some cases. After removing those results which appear for obvious reasons to be inaccurate, the author calculates the most probable values of the heat of combustion and finds the following values: benzoic acid, 6320 $\text{cal.}_{15°}$/gram (vacuum)=26444 joule/gram (vacuum); naphthalene, 9617 $\text{cal.}_{15°}$/gram (vacuum)=40239 joule/gram (vacuum) and sucrose 3949 $\text{cal.}_{15°}$/gram (vacuum)=16523 joule/gram (vacuum), from which the ratios: naphthalene/benzoic acid=1·5217 and sucrose/benzoic acid=0·6248 are obtained. The above figures are probably accurate to 1·5%. The author suggests that the determination of the water value of a calorimetric bomb should be made with all three substances, using the above values and the mean of the three values taken as the correct value. J. F. S.

Heats of Dilution and the Specific Heats of Dilute Solutions of Nitric Acid and of Hydroxides, Chlorides, and Nitrates of Lithium, Sodium, Potassium, and Cæsium. THEODORE W. RICHARDS and ALLAN WINTER ROWE (*J. Amer. Chem. Soc.*, 1921, **43**, 770—796).—The heats of dilution of nitric acid, of the hydroxides of lithium, sodium, and potassium, and of the chlorides and nitrates of lithium, sodium, potassium, and cæsium have been determined at about 16° and 20°. The values obtained are recorded in two long tables in joules and calories. Approximate values are obtained for rubidium compounds by extrapolation. Some of these heats of dilution are negative and some positive. Sodium hydroxide and nitric acid show change of sign on progressive dilution. Distinct relationship to the periodic system is shown in the progression of values, but some eccentricities, particularly in sodium salts, are manifest. From the results, the temperature coefficients of the heats of dilution were found and are recorded both in calories and joules. They are all positive. The specific heats of the various solutions are calculated, and it is shown how, by a simple method of plotting the heat capacity changes, all intermediate solutions may likewise be determined with considerable accuracy. The loss of heat capacity on dissolving salts in water is shown to be of the same order as the gain of heat capacity on neutralising acids by alkalis, in such a sense that the heat capacity is diminished by 50 to 100 mayers by such fraction of each gram ion as is formed from a gram-molecule in solutions containing $100H_2O$. Presumably the nature of the ion determines the exact magnitude of this loss of heat capacity. Heats of dilution and changes of heat capacity are shown to afford a possible partial clue to the extent of electrolytic dissociation. The temperature coefficient of the heat of neutralisation of solutions containing $100H_2O$ is shown to vary somewhat with the nature of the alkali and of the acid, and to average about 51 cal. or 213 joules per degree. Therefore the gain of heat capacity on neutralisation is 213 mayers. J. F. S.

Mass Effect in the Entropy of Solids and Gases. WENDELL M. LATIMER (*J. Amer. Chem. Soc.*, 1921, **43**, 818—826).—A theoretical paper in which it is postulated that there is a certain limiting value of the constraints in a solid below which the effect of the constraints on the entropy of the solid is constant. On this basis, the entropy of solids in which this condition is fulfilled is the sum of the entropies of the elements in the solid. The entropy of the elements in such a solid is given by the equation, $S_{298}=3/2R \log_e$ at. wt. $-0{\cdot}94$. The entropy of all compounds on which data are available, 18 in number, is found to agree with the equation with an average variation of 0·7 entropy unit. The one condition is that the Kopp's law constant for the elements in the compound shall have reached approximately the value 6. The data on 10 diatomic gases are considered in connexion with the equation $S_{298}=3/2R \log_e$ mol. wt. $+R/2 \log_e$ at. wt.′ $+R/2 \log_e$ at. wt.″ $+30{\cdot}22$. With the possible exception of iodine, the agreement is within the limits of experimental error. J. F. S.

Principle of Similitude and the Entropy of Polyatomic Gases. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 866—875).—A theoretical paper in which the theory of similitude or relativity of size is considered by a somewhat simpler method than that previously adopted (A., 1920, ii, 468). The author derives equations connecting the entropy of a perfect gas composed of rigid diatomic or polyatomic molecules, with temperature, pressure, molecular weight, and the moments of inertia of the molecule. These equations are compared with the equations of Sackur, Tetrode, Schames, and Latimer and also with the available experimental data. J. F. S.

Molecular State of Water Vapour. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1921, **43**, 851—857).—The density of saturated water vapour has been recalculated by means of the Clausius-Clapeyron equation for various temperatures, using modern data for the several factors involved. It is shown that the density does not become less than the ideal value below 30°, and that there is therefore no foundation for the hypothesis of spontaneous ionisation. The excess density at 100° computed from Regnault's data is about 100% too large. The numerous and remarkably concordant independent results of Perman (*Proc. Roy. Soc.*, 1903, **72**, 72) and of Krauskopf (*J. phys. Chem.*, 1907, ii, 318) for the vapour pressure of water at about 73° obtained by the gas current saturation method are shown to lead to a vapour density for saturated water vapour at that temperature which is less than 0·1% higher than the ideal value, whilst the value from the Clapeyron equation is 0·9% higher. This discrepancy merits further investigation. If D. Berthelot's equation of state is applied to the mean of these two results for 73°, the numerical basis remaining, from which to postulate polymerisation of water vapour at this temperature, is precisely zero. J. F. S.

Applicability of Mendeléev's Rule in the Case of Benzene and its Halogen-substitution Products. W. HERZ and JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1921, **97**, 381—387).—Making use of the experimental density determinations of benzene and the halogen-substituted benzenes and mixtures of these substances, published previously by Meyer and Mylius (A., 1920, ii, 590) and Herz (A., 1914, ii, 425), the authors have tested the applicability of the Mendeléev rule, $D_t = D_0(1-Kt)$, to these substances. The calculations show that this rule represents the experimental facts equally for normal and abnormal liquids within the limits of the experimental error. The value of K fluctuates irregularly about a mean value, this being probably due to experimental error in the determinations which, since the calculation of K is made from differences, shows itself in an exaggerated manner. From this it follows that the percentage error is of the same order both for normal and abnormal liquids, and the Mendeléev equation cannot be used to differentiate between the two types of liquids. It is possible that a differentiation could be made if the accuracy of the density determinations were increased 10—100 times. It is probable that

the K value of mixtures of normal liquids can be calculated from that of the components of the mixture by the additive mixture rule. J. F. S.

Viscosimeter. ROBERT FISCHER (*Zeitsch. angew. Chem.*, 1921, **34**, 153—154).—Certain modifications are suggested in a falling-sphere viscosimeter described previously by the author (*Chem. Zeit.*, 1920, **44**, 622) for use with dark coloured liquids. The tube is widened so that the tubulus for the thermometer does not interfere with the descent of the ball, and the apparatus is standardised with different sized balls, so that a more equal rate of fall is obtained with liquids of high and low viscosities. In dealing with aqueous solutions, the electrical contacts at the bottom of the tube may be covered with a layer of carbon tetrachloride before the solution is introduced. W. P. S.

Viscosity and Flocculation of Coarse Suspensions. HANS EGNÉR (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1920, **4**, No. 4, 1—25).—The viscosity formula of Arrhenius (A., 1917, ii, 130) does not hold for suspensions of China clay and infusorial earth. It was not possible to test its validity for graphite. The empirical formula of Bingham and Durham (A., 1911, ii, 968) agrees in some cases, but not in others. The effect of electrolytes on the state of coarse suspensions is very marked. Kations flocculate, and increase the viscosity and sedimentation height. Anions act in the opposite way. The magnitude of the flocculating power generally follows the valency rule, but hydroxide ions often act irregularly. The properties of suspensions are very similar to those of suspension colloids. J. R. P.

Influence of some Compounds on the Viscosity of Solutions of Dextrose in Water. SVETOZARA VARIĆAK (*Rev. Chim.*, 1921, **1**, 57—71).—The author records a set of measurements of the coefficient of viscosity, at temperatures between 5° and 40°, of solutions in water of hydrochloric acid, potassium hydroxide, tartaric acid, acetamide, and dextrose, and for mixtures of solutions of dextrose with solutions of each of the other four substances, the concentrations ranging from one to one-tenth gram-molecule of each solute per litre. In all cases the general tendency is for the viscosity to decrease with rising temperature, but, in the neighbourhood of 25°, there is usually a fairly abrupt change in the direction of the viscosity–temperature curve. Thus the viscosities of mixtures of solutions of acetamide and dextrose decrease rapidly with rising temperature from 5° to 25°, but remain nearly constant from 25° to 40°. In most other instances, the fall of viscosity from 5° to 25° is relatively slight, but a rapid fall takes place between 25° and 40°, the viscosities at this temperature for corresponding concentrations being in all cases of about the same magnitude. C. K. I.

Sorption of Iodine by Carbon. JAMES BRIERLEY FIRTH (*Trans. Faraday Soc.*, 1921, **16**, 434—452).—The sorption of iodine by different forms of carbon from solution in benzene and chloroform

respectively has been studied over periods of time extending to five years. The forms of carbon used were lampblack, sugar-carbon, blood charcoal, animal charcoal, and coconut charcoal both from the fruit and the shell, definite weights of which, after suitable heating, were shaken in a thermostat at 25° with a decinormal solution of iodine in the solvent. From the results obtained, the constants β and P are calculated in the formula $x/m=\beta(a-x/v)1/P$, where x is the amount of iodine sorbed by m grams of carbon, and a is the total iodine originally present. Graphically, the results of the experiments are shown by plotting $\log x/m$ against $\log (a-x)$. Generally, a rapid condensation of the iodine by the charcoal takes place in the first few minutes, and is followed by a much slower sorption continuing for months or years. The first condensation is attributed to true adsorption, the second to a slow absorption. The amount of sorption varies from about 90% of the total iodine present in the case of blood charcoal, using chloroform as solvent, to less than 3% with powdered coconut fruit charcoal. The difference is not to be attributed to difference in surface area, but to a specific difference in the form and action of the carbon in the different cases. The amount of sorption is always greater from chloroform than from benzene, in which iodine has a greater solubility. During the second absorption phase the concentration of the iodine in the solvent diminishes to a certain minimum value, after which the rate of change of concentration, whatever the mass of sorbing solid present, is so slow that the concentration appears constant. The initial adsorption velocity is greater the smaller the size of carbon particles, whilst the presence of water in the carbon diminishes its activity. E. H. R.

The Estimation of the Adsorbing Power of Charcoal. I. M. Kolthoff (*Pharm. Weekblad*, 1921, **58**, 630—656).—In order to determine whether the adsorptive power of charcoal of any particular variety for materials in general can be deduced from the adsorptive power for a selected material, experiments were carried out with various kinds of charcoal, iodine, phenol, mercuric chloride, mercuric cyanide, arsenic trioxide, various colouring materials and several alkaloids being employed as materials to be adsorbed. The charcoals selected were norit (water 11·8%, ash 5·7%), bactanate (water 26·3%, ash 7·8%), blood charcoal (water 30%, ash 4·8%), vegetable carbon (water 25·5%, ash, 4·5%), and medicinal carbon (water 30·6%, ash 6·5%), the last three being Merck's preparations. The adsorptive power of each of these varied considerably, but with all the materials tested the order was practically the same, namely, blood charcoal > vegetable carbon = medicinal carbon > bactanate > norit. These results confirm Freundlich's rule that the order in which materials are adsorbed is almost independent of the nature of the solid phase. The quantities adsorbed were only slightly affected by previous treatment of the charcoal with water or acid.

The quantity of iodine adsorbed per gram of charcoal was in the case of norit independent of the end concentration, but diminished with this for the other charcoals, although in no case was the ad-

sorption isotherm $x/m = \alpha c^{1/n}$ found to hold. With almost all the other materials this equation was found to govern the quantities adsorbed, the constant α being taken as an index of the adsorptive power. As a practical method for testing the adsorptive powers of any given charcoal, the determination of the amounts of mercuric cyanide or phenol adsorbed by 1 gram from 100 c.c. of $N/10$-solution is recommended, the result being taken in conjunction with the figures given in the paper. S. I. L.

Critical Study of the Capillary Rise Method for Determining Surface Tension, with Data for Water, Benzene, Toluene, Chloroform, Carbon Tetrachloride, Ether, and Dimethylaniline. II. THEODORE W. RICHARDS and EMMETT K. CARVER (*J. Amer. Chem. Soc.*, 1921, **43**, 827—847. Compare A., 1915, ii, 522).—It is shown that the supposed finite contact angle (reputed to be the weakest point in the capillary rise method) does not exist with the liquids studied in the present work if the glass is properly cleaned and if evaporation of the liquid is prevented. The correction for the capillary rise in the wide tube calculated by Rayleigh and Laplace has been experimentally verified. A preliminary experimental curve for the capillary rise in tubes that are not wide enough to come under these mathematical equations has been obtained. This curve fits smoothly between the theoretical curve for very wide tubes and the theoretical curve for very narrow tubes. It has been shown that the method of calibrating tubes by weighing a mercury thread is not affected to an important extent by a film of air between the mercury and the glass, except perhaps in very fine capillaries. The disturbing effect of ellipticity in the cross section of the capillary is indicated. The difference between capillary rise in air and in a vacuum has been determined for six liquids. In most cases the effect on the surface tension is less than 0·5%. The surface tensions of water, 72·73; benzene 28·88; toluene 28·43; ether 16·96; chloroform 27·14; carbon tetrachloride 26·77; and dimethylaniline 36·56 have been measured in the presence of air. Removal of air increases the surface tension as follows: water +0·02; benzene +0·14; chloroform +0·10; carbon tetrachloride +0·18; ether +0·05; dimethylaniline +0·10. J. F. S.

Kinetic Theory of Osmotic Pressure. KARL F. HERZFELD (*Ann. Physik*, 1921, **64**, 646—660. Compare Jäger, A., 1913, ii, 762).—A theoretical paper in which an attempt is made to ascertain the mechanism of the process which drives a solvent through a semi-permeable membrane into a solution when both are exposed to the same external pressure. The author first considers how the external pressure arises in a pure liquid and then applies the results thus obtained to solutions in which there is no force of attraction between the solvent and the dissolved substance. It is shown that the presence of such an attractive force would not change the osmotic pressure in any sense. When the force of attraction is sufficiently large, the kinetic energy of the dissolved substance acts on the

capillary layer of the solvent instead of on the free surface. It is this pressure which brings about the movement of the surface and thereby the penetration of the solvent through the semi-permeable membrane. The force of attraction causes an increase in the internal pressure of the solution, but this is not in agreement with Tammann's results, as is to be expected from the measurements of the heat of hydration. J. F. S.

Solubility of Naphthalene in Aqueous Solutions of Alcohols and Fatty Acids. JOHANNE CHRISTIANSEN and SVANTE ARRHENIUS (*Med. K. Vetenskapsakad. Nobel-Inst.*, 1920, **4**, No. 2, 1—25).—The object of the investigation was to find a connexion between the ballograms (A., 1913, ii, 97, 177; 1916, ii, 75; 1917, ii, 404) of aqueous solutions of alcohols and fatty acids and other properties of the solutions. The concentration of solvent, alcohol or fatty acid, which exactly dissolves a given amount of naphthalene was determined. The solubility was found to increase as the nth power of the concentration of the solvent in its mixture with water. The value of n is nearly independent of temperature between 0° and 25° and lies between 2 and 4 for different solvents. Acetic acid behaves irregularly, as its value of n changes from 3 below 50 mol.% to 4 above this concentration, which probably indicates a hydrate of the composition $CH_3 \cdot CO_2H,H_2O$ if enough water is present. The solubility curves converge towards the origin, which indicates that the solubility of naphthalene in pure water is practically zero. J. R. P.

Existence of Hydrates in Aqueous Solutions. A. SMITS, L. VAN D. LANDE, and P. BOUMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 969—974).—With the object of finding evidence in favour of the existence of hydrates in aqueous solution, the authors have examined the specific gravity, surface tension, and refraction of solutions of hydrated salts at constant temperature, but these results furnish no evidence in support of the existence of hydrates. In the case of viscosity measurements, however, the authors find support for the view that hydrates exist in solution. The viscosity of ferric chloride solutions has been examined at 40°. This temperature was chosen because it lies very near to the melting points of $FeCl_3,12H_2O$ and $FeCl_3,7H_2O$, and at this temperature the hydrates, if they exist at all, would not be so much dissociated as would be the case at higher temperatures. The viscosity curve is found to rise steadily until the composition has nearly reached that of $FeCl_3,12H_2O$, where a maximum is reached, it then falls until the composition has passed that of $FeCl_3,12H_2O$, and then rises rapidly. This peculiar shape is explained in such a way as to point to the existence of the hydrate in solution. Similar experiments are made in the system H_2O–SO_3, and here a similar curve is obtained at 15° for the hydrate H_2SO_4,H_2O; when the same mixtures are examined at 40° and 60° similar but very much less pronounced curves are obtained, which point to the dissociation of the hydrate at these temperatures. J. F. S.

The Existence of Compounds in Liquid Mixtures. W. P. JORISSEN (*Rec. trav. chim.*, 1921, **40**, 281—284).—The results of Smits, van der Lande, and Bouman (preceding abstract) on the presence of hydrates in aqueous solution as indicated by viscosity measurements on aqueous solutions of ferric chloride and of sulphuric acid and those of other workers on the same subject (compare Kremann and Ehrlich, *Sitzungsber K. Akad. Wiss. Wien, math.-naturwiss*, 1907, **116**, II*b*, 789; Dunstan and Wilson, T., 1907, **91**, 83; 1908, **93**, 2179) are discussed as part of the more general question of the existence of compounds in liquid mixtures. W. G.

The Saturated Solutions of Two or several Substances. Application of Le Chatelier's Law. C. RAVEAU (*Compt. rend.*, 1921, **172**, 1099—1102).—The author discusses the law of reciprocity and considers that a careful revision will result in the correction of certain data, with reference to the solution of salts in the presence of one another, which are at present in contradiction with this law. W. G.

Surface Forces with Hetero-polar Crystal Lattices. Adsorption of Lead Isotopes by Colloidal Silver Haloids. K. FAJANS and K. VON BECKERATH (*Zeitsch. physikal. Chem.*, 1921, **97**, 478—502).—The type of adsorption, which consists in the accumulation of dehydrated solution ions on the oppositely charged ions of a crystal lattice, is theoretically considered. It is shown from colloid chemical experiments that Paneth's adsorption rule for the adsorption of radio-elements in all probability is true for the present type of adsorption (A., 1914, ii, 19). The adsorption of thorium-*B* by silver bromide sols, and by silver chloride and iodide, has been experimentally determined, as has also that of ordinary lead by negative silver bromide sols. The results show that silver haloid sols, which have become positively charged by the adsorption of silver ions, do not adsorb thorium-*B* to a measurable extent. Negatively charged silver haloid sols adsorb thorium-*B*, and the amount of adsorption increases with increasing excess of the halogen ion. Negatively charged silver bromide sols adsorb quantities of lead up to a concentration $0{\cdot}25\times10^{-3}$ millimols./litre $(Pb(NO_3)_2$ in strict proportion to the lead concentration. At higher concentrations, the adsorbed amount falls short of the strict proportionality. J. F. S.

A Thermo-electrical Differential Method for the Determination of Transition Points of Metals at Comparatively Low Temperatures. A. SMITS and J. SPUYMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 977—979. Compare this vol., ii, 246).—Making use of the method previously described and of a still more sensitive modification of the method, an attempt was made to ascertain whether copper shows a transition point at about 70°, but although every possible means were taken to bring about transition, no indication is given of such a point by either method. J. F. S.

Formation and Stability of Modifications of Polymorphous Substances Below their Transition Temperature. R. Brauns (*Centr. Min.*, 1921, 225—229).—The metastable forms of sulphur, including monoclinic prismatic sulphur, which form when molten sulphur crystallises, can be kept unchanged for years between a microscope slide and cover-glass. Other metastable crystals which can be obtained and preserved are the yellow form of mercuric iodide which is stable only for a few hours, and the rhombohedral form of potassium nitrate, which may be kept for years. These substances when crystallising appear to follow Ostwald's step rule, that when a change of form occurs, the form appearing is that which is accompanied by the smallest loss of free energy. Doubly-refracting cubic crystals of boracite found in salt deposits indicate that the boracite first crystallised in the cubic form far below its transition point, 265°. Mügge's conclusion that the temperature rose locally to so high a point as this during crystallisation is not justified; more probably this substance also follows Ostwald's rule, and separates first in the metastable cubic form. E. H. R.

Thermo-kinetic Explanation for the Reciprocal Attraction of Colloidal Particles (A Possibility of Explaining Gravitation). Robert Fricke (*Zeitsch. physikal. Chem.*, 1921, **97**, 464—466).—A correction and an extension of the author's previous paper (A., 1920, ii, 740). J. F. S.

The Soaps as Protective Colloids for Colloidal Gold. Thomas Iredale (T., 1921, **119**, 625—634).

Colloid Chemical Aspects of the Theory of Indicators. G. Wiegner (*Mitt. Lebensm. Hyg.*, 1920, **11**, 216—227).—Many indicators are known to possess colloidal properties, being usually negatively charged suspensoids of which the degree of dispersion depends on the hydrogen-ion concentration. Congorubin in acid solution forms larger particles than in alkaline solution, and conforms with Ostwald's rule that increase in the size of the particles shifts the colour towards the blue end of the spectrum. Salts tend to give the blue colour, the effect increasing with the valency of the kation, in agreement with Schulze's rule. With barium hydroxide the colour remains blue, since the influence of the bivalent positive ion is greater than that of the univalent negative ion. Emulsoids such as casein, gelatin, etc., exert a protective action similar to that on colloidal gold, which then behaves as a synthetic indicator. The "protein errors" of indicators and their sensitisation by salts admit of explanation from this point of view. Chemical Abstracts.

Phthalate Buffers—Some Incompatibilities. Harper F. Zoller (*J. Amer. Chem. Soc.*, 1921, **43**, 914—916).—When a 0·1% solution of pure crystal-violet (hexamethyltriaminotriphenylmethane chloride) was added to a set of Clark and Lubs buffer mixtures throughout the range P_H 1·0 to 10·0 precipitation was found to occur in the zone P_H 2·2 to 4·4, and the amount of precipitate settling out seemed to bear a direct relation to the amount of dissociated free phthalic acid present. This did not occur when

buffer solutions over a similar range were prepared from acetic, citric, tartaric, or propionic acids. The phenomenon is due to the formation of an additive compound of phthalic acid with the triphenylmethane dye.

Impure lactalbumin in dilute concentration (0·01—0·001%) does not coagulate or flocculate at 60° in either citrate or acetate buffers, but it does in phthalate buffers over the range P_H 2·4 to 5·0. W. G.

The Influence of Salts on Chemical Equilibria in Solution. J. N. Brönsted (T., 1921, **119**, 574—592).

Equilibria in Condensed Systems. Alfred Schulze (*Zeitsch. physikal. Chem.*, 1921, **97**, 388—416).—Vapour pressure measurements of mixtures of ethyl ether–benzene, benzene–chloroform, and acetone–ethyl ether, of various compositions, made at a series of temperatures show in the first two cases that the components enter into chemical combination in the molecular ratio 1 : 1, and these compounds exist in a dissociated condition in the mixtures. The measurements for mixtures of ethyl ether–acetone show that acetone is a complex liquid. Calculation shows that at 20° it is bimolecular, whilst at 0° the molecule is very much more complex. The molecular constitution of the above-named mixtures has been calculated by the aid of the law of mass action, and it is shown that from a knowledge of this composition the other physical properties of the mixtures may be calculated from the corresponding properties of the components. This has been done for the specific heat and the molecular refraction, and the calculated values have been compared with the experimental values. A very good agreement between the two sets of values is found. J. F. S.

The Pressure Variation of the Equilibrium Constant in Dilute Solution. A. M. Williams (*Trans. Faraday Soc.*, 1921, **16**, 458—463).—The expression obtained by Planck for the variation of the equilibrium constant of a reaction in dilute solution with pressure is $\partial \log K/\partial P = V_1 - V_2/RT$, where K is calculated for concentrations which are molar fractions of the total number of mols. present, including the solvent, and $V_1 - V_2$ denotes the volume change during the reaction. Rice (*Trans. Faraday Soc.*, 1917, **12**, 318) obtained a similar expression, but his K referred to volume concentrations. An attempt to explain the discrepancy was made by Mazzucchelli (A., 1920, ii, 17), but the explanation offered by him is now shown to be untenable. It is shown that the discrepancy is due to the different interpretations put upon the term $(V_1 - V_2)$ by Rice. Denoting Rice's constant by K', it is shown that $\partial \log K'/\partial P = \partial \log K/\partial P - \Sigma\lambda\beta$, where β is the compressibility of the fluid and $\Sigma\lambda$ is the change in the number of molecules involved in the reaction. An independent proof of the theorem from first principles is also presented. E. H. R.

Theory of Chemical Affinity from the Point of View of Polar Dissociation and the Law of Mass Action. D. Reichinstein (*Zeitsch. physikal. Chem.*, 1921, **97**, 257—303).—The normal potentials of the electrodes $Te|Te_2''$ and $Te|Te^{\cdots\cdot}$ have been

experimentally determined at the ordinary temperature. From data obtained the following constants have been calculated: ${}_0\epsilon_{hk}\mathrm{Te} \leftarrow \mathrm{Te}^{\cdot\cdot\cdot\cdot} = +0{\cdot}558$ volt and ${}_0\epsilon_{ha}\mathrm{Te} \rightarrow \mathrm{Te}_2'' = -0{\cdot}827$ volt. The above values are used to calculate the *E.M.F.* of the element $\mathrm{Te}|\mathrm{Te}^{\cdot\cdot\cdot\cdot}||\mathrm{Te}_2''|\mathrm{Te}$ and the value ${}_a\epsilon^0{}_k = 1{\cdot}385$ obtained which is termed shortly the polarity potential. The polar solubility product of the second order is given by $\lambda = (\mathrm{Te}^{\cdot\cdot\cdot\cdot})(\mathrm{Te}_2'')^2 = 6{\cdot}2 \times 10^{-97}$ and the combination constant $K_{20} = (\mathrm{Te}^{\cdot\cdot\cdot\cdot})(\mathrm{OH}')^6/(\mathrm{TeO}'') = 2 \times 10^{-47}$. The polar solubility product of the third order

$$\lambda_3 = (\mathrm{TeO}_3'')(\mathrm{Te}_2'')^2(\mathrm{H}^{\cdot})^6 = \lambda.\lambda_{\mathrm{H_2O}}/K_{20} = 3{\cdot}4 \times 10^{-135}.$$

The theory of chemical affinity is based on the following foundations. First, the total affinity of a chemical element, that is, the sum of its positive and negative affinities, has nothing to do with its position in the electrolytic potential series, and secondly, the polarity potential of a chemical element is a direct measure of its total affinity, and this is therefore a function of its polar solubility product. The following rules concerning the relationships of the normal potentials are deduced from experimental work. When the value of ${}_0\epsilon_{kh}$ is known for a given chemical element, the value of ${}_0\epsilon_{ha}$ will be found to lie in the direction of the less noble elements and vice versa. The author makes the assumption that the chemical elements, which occupy the same sub-group of the periodic system, have the same value for their polar solubility products of the first order. When the electronic dissociation of an element M_2 is considered in connexion with the polar dissociation thus: $M_2 \rightleftharpoons M^{\cdot} + M'$; $M' \rightleftharpoons M + \ominus$, the chemical elements may be completely characterised by the three values λ, δ, and μ. These values are $\lambda = (M^{\cdot}) \times (M')$, $\delta = (\mathrm{M}).(\oplus)/M'$, and $\mu = M.(\ominus)$. The positive, negative, and total affinity of a chemical element can be quantitatively represented by these three quantities. J. F. S.

An Apparatus for Registering Variations of a Gaseous Mass with Time. A. A. GUNTZ (*Compt. rend.*, 1921, **172**, 918—920).—The apparatus which is figured and described consists essentially of a reaction vessel containing the gas the variations in volume of which is to be observed (for example in the reduction of an oxide by hydrogen), connected to a volumeter, having a nickel-chrome wire passing along its axis. Variations in volume are indicated by variations in the resistance of this wire as more or less of its length is free from the mercury. W. G.

Kinetics of the Decomposition of Hydrogen Peroxide. FR. BÜRKI and FR. SCHAAF (*Helv. Chim. Acta*, 1921, **4**, 418—425).—Investigation of the velocity of decomposition of hydrogen peroxide in alkaline solution under different conditions shows that this reaction is of the first order. The velocity of the reaction is dependent on the concentration of the base, but independent of its nature, and appears to be conditioned solely by the concentration of the hydroxyl ion. T. H. P.

The Speed of Reaction of Metallic Magnesium in Aqueous Solutions. ANT. VYSKOCIL (*Chem. Listy*, 1920, **14**, 121—123, 142—145, 166—171, 189—191).—On dissolving magnesium in

aqueous solutions of ammonium or neutral metallic salts, the water is first decomposed, a process which is catalysed by anions, particularly chloridion; thereafter the velocity of reaction depends largely on the chemical character of the solution. The Nernst-Brunner equation is inapplicable. The views advanced by Kistiakowsky (A., 1910, ii, 258) are upheld. Metallic magnesium can be rendered temporarily passive for certain reactions.

CHEMICAL ABSTRACTS.

Some Physico-chemical Problems connected with the Stability of Explosives. CYRIL NORMAN HINSHELWOOD (T., 1921, **119**, 721—734).

The General Study of Catalysis. MARCEL GUICHARD (*Bull. Soc. chim.*, 1921, [iv], **29**, 212—214).—The author indicates lines of research on catalysis in heterogeneous media, which are desirable in order that information may be obtained as to the mechanism of the action.

W. G.

Catalytic Action and Micellar Magnitude (Degree of Dispersion). ANTONIO MADINAVEITIA and FERNANDO DIÁZ AGUIRRECHE (*Anal. Fís. Quím.*, 1921, **19**, 124—135).—The authors have studied the relation between catalytic power and degree of dispersion in the rate of decomposition of hydrogen peroxide by colloidal gold solutions. By addition of suitable quantities of calcium chloride solution, gradual coagulation was effected as shown by colour changes in the metallic sol. Catalytic power was found to increase to a maximum, followed by a decline. The maximum catalytic power was observed when the gold sol was violet in colour. A similar result was obtained using dilute sulphuric acid as coagulant. The fact that catalytic power may sometimes increase with increasing micellar magnitude might be inferred from the fact that metallic ions on the one hand and macroscopic fragments of metal on the other possess little or no catalytic activity. An initial depression in catalytic power observed in these experiments is referred to the saturation of the liquid with oxygen in the early stages of the reaction. After previously saturating with oxygen, the initial value of K was lower and remained steady. G. W. R.

Variations in the Catalytic Power of Colloidal Systems. ANTONIO DE GREGORIO ROCASOLANO (*Anal. Fís. Quím.*, 1921, **19**, 114—124. Compare this vol., ii, 251).—The ageing of colloidal systems has been studied in the variations of their catalytic power. The decomposition of hydrogen peroxide was followed, using as catalyst platinum electrosols of different ages and of different concentrations. In all cases the catalytic power, expressed by the constant K for the unimolecular reaction, showed an initial increase followed by a gradual decrease. Similar results were obtained with palladium sols. The initial increase of catalytic power with age was also shown in the case of the inversion of sucrose by invertase. The catalytic power of metallic sols is supposed to reside in the metal-oxygen complex and the initial increase in activity is attributed to an increase of oxygen concentration in the

disperse phase. With progressive ageing, the degree of dispersion diminishes and the catalytic power passes through a maximum and declines. Certain indications of periodicity in the decline of catalytic power were obtained. G. W. R.

Catalysis. XII. Some Induced Reactions and their Mechanism. NIL RATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 1074—1079. Compare this vol., ii, 36—37).—A number of oxidations which are not readily brought about by oxygen directly, but are accelerated by the addition of a reducing agent which is easily oxidised by free oxygen, are described and discussed. Of these the oxidation of sodium arsenite by oxygen in the presence of sodium sulphite is an example. In this case sodium arsenite is not appreciably oxidised by oxygen, but sodium sulphite is; adding sodium sulphite to the arsenite accelerates the oxidation of the arsenite, but at the same time the oxidation of the sulphite is retarded. It is found in all cases that the substance, in which the oxidation is induced, acts as a negative catalyst towards the substance which induces the oxidation. To explain this action, the author assumes that a complex of the two oxidisable substances must be formed and that of this complex the part composed of the less oxidisable substance is more easily oxidised. J. F. S.

Catalytic Oxidation of Ferrous Salts in Acid Solutions. RICHARD THOMAS and EDWARD THOMAS WILLIAMS (T., 1921, **119**, 749—758).

Certain Catalytic Reactions. A. MAILHE (*Caoutchouc et Guttapercha*, 1920, **17**, 10584—10585; from *Chem. Zentr.*, 1921, i, 717).—Many syntheses effected by catalytic means are reversed at higher temperatures. The union of sulphur dioxide and oxygen which takes place readily at 400° in the presence of platinum black takes place more slowly at 500° on account of incipient reversal. *cyclo*Hexane, formed from benzene and hydrogen at 180° in the presence of nickel, decomposes again at 300°, forming benzene and hydrogen. Aldehydes and ketones give primary and secondary alcohols with hydrogen at 150—180° in the presence of nickel: these decompose again at 250° with the formation of aldehydes or ketones and hydrogen. The formation of amines from nitriles and hydrogen and the formation of nitriles from acids and ammonia are similarly reversible. Phenol and ethyl alcohol, in the presence of thorium oxide at 400°, give phenetole; at 460°, in presence of steam, the phenetole decomposes into phenol and ethyl alcohol.

[With DE GODON].—A mixture of aniline and methyl alcohol gives, at 380—400° in the presence of aluminium and thorium oxides, dimethylaniline, which at 460—480°, in the presence of thorium oxide and steam, gives aniline and methyl alcohol. G. W. R.

A Catalytic Method of Hydrogenation. JEAN NIVIÈRE (*Bull. Soc. chim.*, 1921, [iv], **29**, 217—219).—The material to be hydrogenated is dissolved in a suitable solvent in a stout-walled bottle,

a small amount of a solution of palladium chloride or platinum chloride is added to act as a catalyst, and then the calculated amount of calcium hydride is added gradually, the flask being stoppered and well shaken. This method was successfully used for the reduction of benzaldehyde, nitrobenzene, and benzylideneacetone. W. G.

Heterogeneous Catalysis and Adsorption. H. R. KRUYT and C. F. VAN DUIN (*Rec. trav. chim.*, 1921, **40**, 249—280).—The velocity of reaction in the case of certain chemical changes has been determined in the absence and in the presence of charcoal as an adsorbing agent. The velocities of hydrolysis of ethyl acetate, and of the sodium salt of methyl *p*-sulphobenzoate, the rate of fixation of bromine by sodium hydrogen *p*-sulphocinnamate, and the rate of decomposition of the sodium salts of *p*-sulphodibromohydrocinnamic acid are all diminished by the presence of charcoal. On the other hand, the reaction between potassium iodide and dibromopropionic acid is accelerated by the presence of charcoal.

The adsorption of these reacting substances alone or in the presence of the products of reaction has been examined. In most cases the adsorption is favoured by the presence of the products of reaction, but the results do not permit of the deduction of any definite theory as to the kinetics of the reactions. The results show that heterogeneous catalysis is not entirely due to an increase in the active mass, consequent on an increase of the concentration in the limit layer. This increase in the concentration may be equally well accompanied by an increase or a diminution in the velocity of the reaction, according as the adsorbed reagents are in a more or a less advantageous position. The results are discussed in the light of the theories of Langmuir (A., 1917, ii, 19, 525) and of Harkins (A., 1917, ii, 238, 239) with which they are in accord. W. G.

The Influencing of the Activity of Catalysts. II. Reduction of Acid Chlorides to Alcohol and Ester. KARL W. ROSENMUND, F. ZETZSCHE, and F. HEISE (*Ber.*, 1921, **54**, [*B*], 638—647).—In a previous communication (this vol., ii, 320) it has been shown that the catalytic reduction of acid chlorides can be so influenced by the addition of suitable substances that it ceases at the aldehyde stage; it is now demonstrated that such control can be so exercised that it proceeds to the next stage, namely, the formation of alcohol (which reacts with the excess of acid chloride) to yield the ester.

The reduction of benzoyl chloride by hydrogen and palladium in boiling xylene solution gives hydrocarbons of high boiling point (chiefly dibenzyl, about 45%), benzoic acid (16%), benzyl benzoate (15%), together with volatile substances such as toluene. Diminution of the partial pressure of the hydrogen increases the yield of ester from 15% to 37% and decreases that of complex hydrocarbons from 45% to 22%. The effect of specific addenda is described, the substances chosen being such as contain an element of varying valency; minute amounts of quinoline alter the course of the

reaction completely, the product being benzyl alcohol containing small amounts of benzaldehyde and dibenzyl ether, whereas hydrocarbons, benzoic acid, and benzyl benzoate are completely absent. Xanthone, on the other hand, has a purely quantitative effect, inducing a diminution in the production of complex hydrocarbons and an increase in acid and ester. The co-existence of the two latter substances is a result of the fission of the ester into acid and toluene under the influence of hydrogen. This action can be excluded by the addition of quinoline or, preferably, of toluene; the effect is not due to a lowering of the temperature of reaction, since it is very pronounced in the presence of xylene under the same conditions.

By a suitable combination of the actions of toluene and xanthone, suitable conditions are established for the production of ester as main product of the reaction. The presence of the latter prevents the catalyst from bringing about the reduction of alcohol to hydrocarbon whilst allowing the conversion of the acid chloride to aldehydes and alcohol. Toluene behaves as anti-ferment towards the reductive ester fission. H. W.

The Influencing of the Activity of Catalysts. III. Oxidative Catalytic Dehydrogenation of Alcohols. I. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1921, **54**, [*B*], 1092—1098. Compare this vol., ii, 320, and preceding abstract).—The catalytic oxidation of a primary alcohol may lead to the production of (1) aldehyde, (2) acid, (3) ether, and (4) condensation products. The reaction has been studied in the case of benzyl alcohol under conditions which do not necessitate vaporisation and with the object of limiting the scope of the change to the production of benzaldehyde. Benzyl alcohol gives only about a 3% yield of the latter when oxidised by oxygen in boiling cumene solution, and this yield is not very greatly increased in the presence of copper, silver, magnesium, platinum, nickel, aluminium, zinc, antimony, or carbon. Amongst these almost equivalent catalysts, selective action can be induced in the cases of copper, nickel, and silver by the suitable addition of quinoline, the production of benzaldehyde being favoured in the case of copper and of ether and condensation products in the cases of nickel and silver, thus affording an example of the transformation of slightly active catalysts into powerful and specific substances. The dehydrogenating action of catalytically excited oxygen and of nitro-groups is additive; the latter are preferably introduced in the form of *m*-dinitrobenzene. The best yields of aldehydes from alcohols are obtained by the catalytic oxidation of an equimolecular mixture of alcohol, quinoline, and *m*-dinitrobenzene in cumene solution in the presence of copper.
H. W.

Mass-spectra and Atomic Weights. A Lecture delivered before the Chemical Society on April 7, 1921. By FRANCIS WILLIAM ASTON (T., 1921, **119**, 677—687).

Diameter of the Atoms. WILHELM H. WESTPHAL (*Zeitsch. Physik*, 1921, **4**, 254—256).—A theoretical paper in which on the basis of Rankine's explanation of the difference between the radii of the inactive gases and the halogens as found by Bragg from the crystal structure method and those found by the viscosity method, the author shows that it is possible to calculate the constants of the repulsion law (A., 1920, ii, 679). The values of $\log_{10} a+8$ are plotted against $\log_{10} a/r_0$ where a is the radius of the molecule and $2r_0$ the smallest distance between the molecules. The curves are practically straight lines in both cases. J. F. S.

Theory of Valency. I. The Behaviour of Decolorised Magenta Solutions. II. The Configuration of Benzene and the Organic Hydroxyl Group. JULIUS GNEZDA (*Rev. Chim.*, 1921, **1**, 17—23, 33—40).—Organic substances of many widely varying types (amides, amines, amino-acids, cyanogen compounds, aldehydes, proteins, etc.) generate a red colour with magenta solutions which have been decolorised by means of sodium sulphite or magnesium metal, the development of the colour usually taking place more easily when magnesium is the decolorising agent than when sodium sulphite is used. In certain instances, a colour is developed with magnesium–magenta solutions whilst no colour is formed with sulphite–magenta solutions. In order to explain these and similar facts, the author develops a theory of valency in which oxygen is considered to possess, besides its two principal valencies, two stronger and two weaker subsidiary valencies, which, in certain circumstances, radiate "ponderable or imponderable" matter into the surrounding space and may bring about reoxidation of the decolorised solution.

In the second paper, the author develops formulæ for various compounds in accordance with this theory. C. K. I.

Theory of Ammonium Salts and Co-ordination Compounds in Organic Chemistry. JEAN PICCARD and JEAN HENRI DARDEL (*Helv. Chim. Acta*, 1921, **4**, 406—417).—The authors discuss the central and co-ordination formulæ for ammonium chloride and similar compounds, and demonstrate that the hypothesis of the central formula, which has lost ground in inorganic chemistry, receives even less support from organic chemistry. A doubly-linked atom often occupies two co-ordination places, this being the only explanation possible for the isomerism of fumaric and maleic acids or of the oximes. On the other hand, it may readily be assumed that a doubly-linked radicle may be displaced by another radicle from one of its co-ordination positions and yet remain doubly linked electronically. According to this view, if the number of radicles grouped round the central element of a compound is smaller than the co-ordination number of such element, the latter is co-ordinately unsaturated.

In support of the above theory, it is pointed out (1) that ethylene is co-ordinately unsaturated, giving with water a crystalline compound differing from alcohol, and (2) that liquid ethylene and liquid hydrogen chloride are miscible in all proportions with develop-

ment of heat. The central formula is rendered applicable to oxonium and iodonium salts only by the introduction of arbitrary hypotheses, and becomes quite inadmissible as a means of expressing carbonium salts of the type described by Kehrmann and Effront (this vol., i, 348), for the reason that an element of the fourth group of the periodic system can only be quadrivalent.

As regards saturation, compounds may be divided into four classes : (1) Those unsaturated both electronically and co-ordinately, such as the unstable compounds, ferrous chloride, sulphur dioxide, nitrosobenzene, and triphenylmethyl. (2) Those unsaturated electronically, but saturated co-ordinately. Inorganic compounds of this type are often highly stable; there are but few organic compounds in this class, and potassium ferrocyanide, the additive compound of triphenylmethyl and ether, may be cited. (3) Compounds electronically saturated but co-ordinately unsaturated : silver chloride, calcium chloride, sulphur trioxide, ammonia, etc.; also aniline, dimethylaniline, nitrobenzene, *p*-benzoquinone, *p*-benzoquinonedi-imine and its hydrochloride, quinol, acetone, probably all unsaturated hydrocarbons and their derivatives, etc. (4) Compounds saturated from both points of view : cryolite, salts of metals with their maximum valencies and with water of crystallisation, methane, carbon tetrachloride, etc.

The cases of the atoms of nitrogen, carbon, sulphur, oxygen, and platinum are discussed, and the conclusion is drawn that the co-ordination positions are pre-existent in the atom. T. H. P.

Graphical Methods (Nomograms) for Chemical Calculations. J. BABINI (*Anal. Assoc. Quím. Argentina*, 1921, **9**, 34—43).—In the calculation of results which are functions of two or more variables, graphical methods (nomograms) may be conveniently employed. Two nomograms are developed. One is for the estimation of urea in urine, using the formula $0{\cdot}0747x = V/10{\cdot}273/T$ where x is the number of grams of urea per thousand, V the volume of nitrogen in c.c., and T, the absolute temperature. The other nomogram is for the evaluation of $\log a/a-x$ in the study of unimolecular reactions. G. W. R.

Apparatus for Filtration in Anhydrous or Indifferent Gases. ARTUR WOLFRAM (*Ber.*, 1921, **54**, [*B*], 857—859).—The apparatus was primarily designed in connexion with the work of Steinkopf and his co-workers (this vol., i, 404) on the addition of cyanogen bromide to compounds of arsenic; it allows the preparation, filtration, and desiccation of a substance in a single operation and with complete exclusion of moisture. The reaction vessel consists of a round-bottomed flask provided with a tubulus in one side which permits the attachment of a dropping funnel into which a dried gas can be passed as required. The accurately-ground neck of the flask presses a hardened filter-paper against a perforated porcelain disk placed in a filter-tube similar to those used with Gooch crucibles, the junction between the tube and flask being made by a rubber ring. The narrow end of the filter-tube is attached by a two-holed rubber stopper to a separating funnel, the other hole allowing a

connexion to be made to the exhaust pump. The whole apparatus is mounted in a slightly inclined position and the reacting substances are mixed in the flask; it is then brought into a vertical position whereby the reaction mixture flows on to the filter-paper and the precipitate is filtered by suction. The filtrate is run off from the larger funnel and the necessary wash liquid is introduced through the smaller one. The precipitate is ultimately dried by aspirating a current of dry air or other suitable gas through it. H. W.

High Vacuum Methods in Chemistry. M. VOLMER (*Zeitsch. angew. Chem.*, 1921, **34**, 149—151).—The mercury vapour pump has a very high efficiency, and, when used in conjunction with a water-pump, is capable of reducing the pressure in a vessel of 1 litre capacity to 0·1—0·01 mm. within a few seconds. The pump may be used for distillations under low pressure, molecular weight determinations, thermal decompositions, etc. W. P. S.

Inorganic Chemistry.

Colour and Molecular Formula of Water and Ice. I. E. TOMKINSON (*Chem. News*, 1921, **122**, 205—208).—The theories as to the colour of water and ice are reviewed. The colour has been supposed to be due to selective absorption, to scattering by suspended particles, to a sky-effect, and (in the case of sea-water) to organic matter in solution. The first and fourth explanations are believed to cover all the facts. J. R. P.

The Atomic Weight of Chlorine in some Minerals. (MLLE) IRÈNE CURIE (*Compt. rend.*, 1921, **172**, 1025—1028).—The atomic weight of chlorine derived from three different minerals was determined. The values obtained for chlorine derived from a sample of sodalite (sodium aluminium chlorosilicate) from Canada, and from a sample of calcium chlorophosphate from Norway agree with the value for chlorine from sea-water. The value, 35·60, for chlorine from a sample of sodium chloride from a desert region in Central Africa was slightly high. W. G.

The Theory of Electrochemical Chlorate and Perchlorate Formation. N. V. S. KNIBBS and H. PALFREEMAN (*Trans. Faraday Soc.*, 1921, **16**, 402—433).—This paper, which is the outcome of a series of investigations undertaken to obtain data of importance for the technical control of the electrolytic chlorate and perchlorate process, is divided into three parts.

Part I records the results of conductivity measurements of solutions of sodium chlorate, mixtures of chloride and chlorate, perchlorate, and mixtures of chlorate and perchlorate and also the

results of experiments on the dynamics of the conversion of hypochlorite into chlorate. The conductivity of sodium chlorate was determined in solutions containing from 100 to 600 grams per litre between 20° and 80° at 10° intervals, and at higher temperatures than 40° the concentration was increased to 750 grams per litre. For a given concentration, the increase of conductivity with temperature is approximately linear. At constant temperature, the conductivity–concentration curve passes through a maximum which at 20° is at 530 and at 60° is at 600 grams per litre. The conductivities of a wide range of mixed sodium chloride–sodium chlorate solutions were determined between 20° and 80°. In general, with constant chloride, an increase of chlorate concentration at any temperature lowers the conductivity, whilst an increase of chloride with constant chlorate raises the conductivity, except at higher concentrations, where an increase of either salt lowers the conductivity. The conductivities of a limited range of mixed sodium perchlorate and chlorate solutions were determined between 20° and 60°, whilst pure sodium perchlorate solutions were examined only at 20° and 60° in concentrations up to 1100 grams per litre. The conductivity of perchlorate falls off considerably at higher concentrations.

The formation of chlorate from hypochlorite is represented by the equations

$$OCl' + 2HOCl = ClO_3' + 2H^{\bullet} + 2Cl'$$
$$2OCl' + 2H^{\bullet} + 2Cl' = 2HOCl + 2Cl'$$

the net result being the disappearance of three hypochlorite ions with formation of one of chlorate and two of chloride. The second reaction is practically instantaneous, and the first, although apparently termolecular, follows a unimolecular course, since the concentration of hypochlorous acid remains constant. The velocity constant, $k' = 1/t \log_e a/a-x$, where a and x refer to concentration of NaOCl only, was determined between 40° and 80° for different concentrations of hypochlorous acid. The velocity constant increases with increasing concentration of HOCl. The velocity is proportional to the square of the hypochlorous acid concentration, hence $k'/[HOCl]^2$=a constant k. From 60° to 80° k may be represented by the formula $k = e^{0 \cdot 6 + 0 \cdot 056t}$, but at lower temperatures this formula gives too high results.

Experiments are described in which the attempt was made to measure the ohmic resistance and electrode potentials of chlorate and perchlorate cells, but the exact nature of the *E.M.F.* and resistances measured cannot be interpreted.

II. *Chlorate Formation*.—The theory of chlorate formation in the chlorate cell and the sources of loss of efficiency are discussed. In the cell, working normally, an equilibrium is set up in which the hypochlorite formed by the current is equal to that which is being changed to chlorate by the reaction $OCl' + 2HOCl = ClO_3' + 2H^{\bullet} + 2Cl'$. Loss of efficiency may be due to reduction of the oxidised product by cathodic hydrogen or to evolution of anodic oxygen. The former is probably negligible in technical cells; the latter may be due to discharge of hydroxyl ions, of chlorate ions, or of hypochlorite

ions. It is concluded that the discharge of hypochlorite ions is the principal cause of loss of efficiency, the reaction taking place according to the equation $2OCl' + H_2O = 2HOCl + O$. The loss of efficiency may be determined by estimating the quantity of oxygen in the cell gases. It was shown experimentally that, as the hypochlorite-ion concentration was increased by adding sodium hydroxide to a normally running cell to suppress the hypochlorous acid (which has an extremely low dissociation constant), the percentage of oxygen evolved increased in approximately linear proportion to the sodium hypochlorite concentration. The percentage of oxygen evolved decreased when the current density was increased, and vice versa, but after a time tended to return to its original value. An equation is deduced for expressing the efficiency of the cell in terms of hypochlorite concentration and temperature, and the constants of the equation are calculated from experimental results. The energy efficiency of the cell is also discussed.

III. *Perchlorate Formation.*—The theory of electrolytic perchlorate formation from chlorate put forward by Oechsli (A., 1904, ii, 22), and the alternative views of Bennett and Mack (A., 1917, ii, 199), are reviewed. The latter view rejects Oechsli's theory of chlorate-ion discharge and postulates direct oxidation of chlorate by active anodic oxygen. The present authors cannot uphold Bennett and Mack's objections to the discharge of chlorate ions, but, on the other hand, the mechanism of perchlorate formation from the discharged ions proposed by Oechsli appears unnecessarily complicated. Probably the reaction is similar to that of persulphate formation, thus :—$O_2ClO- + -OClO_2 = [O_2ClO-]_2$; $[O_2ClO-]_2 + H_2O = O_2ClO{\cdot}OH + O_2ClOH$. Contrary to what is generally stated, high efficiency can be obtained at as high a temperature as 60° if the current density is sufficiently great. It is shown that chloride may be produced during the electrolysis of chlorate, possibly by the reaction $4HClO_3 = 3HClO_4 + HCl$. The amount of chloride formation increases with temperature, but may be largely prevented by the presence of chromate. The energy consumed in the perchlorate cell is discussed. E. H. R.

Preparation of Fluorine from Molten Potassium Hydrogen Fluoride. FRIEDRICH MEYER and W. SANDOW (*Ber.*, 1921, **54**, [*B*], 759—766).—The method is a development of that proposed recently by Argo, Mathers, Humiston, and Anderson (A., 1919, ii, 333).

The apparatus consists of a cylinder of Acheson graphite which acts as crucible and cathode. It is closely surrounded by a copper cylinder which is electrically heated. The anode is of Acheson graphite, and is made wider at the lower than at the upper end; at the former, six vertical grooves are cut into it to increase the amount of surface exposed. The diaphragm is composed of a copper cylinder to the lower end of which four conical copper rings are successively attached and, finally, a reversed ring fastened to a horizontal piece of copper foil. Details as to structure and insulation are given. Potassium hydrogen fluoride, which forms a clear mobile molten mass at 240°, is used as electrolyte, this being found

preferable to mixtures of the substance with sodium fluoride, sodium hydrogen fluoride, lead fluoride, or strontium fluoride by reason of its greater homogeneity and smaller evolution of hydrogen fluoride. The crucible is slowly heated to a temperature not exceeding 250°, and, since the molten salt obstinately retains traces of water, the electrolysis is commenced with a small current, which is continued until the impurity has been completely decomposed, after which the electrolysis proper is commenced. When the bath has been in use for some time, the temperature may be increased to 270°, but it is not advisable to go beyond this point, as the gas is then liable to carry solid matter with it, and thus to cause a stoppage of the tubes, a leakage of fluorine into the hydrogen, and consequent explosion. For the same reason, when disconnecting the apparatus it is necessary to ensure the escape of the hydrogen before dismantling.

The fluorine evolved at the beginning of an experiment contains considerable quantities of ozone, which practically disappears after one-half to three-quarters of an hour. Any volatilised hydrogen fluoride can be removed quantitatively by passage over granular sodium fluoride. The anode is very slightly attacked, and the gas contains not more than 0·2% of carbon tetrafluoride. The current yield is more than 75% of that theoretically possible. H. W.

The Number of Molecules per Cubic Centimetre of Oxygen obtained by the Dispersion. C. STĂTESCU (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 164—167).—The value of $2{\cdot}73\times10^{19}$ at S.T.P. is deduced by an application of Drude's formulæ. J. R. P.

Tellurium Tetraiodide. A. DAMIENS (*Compt. rend.*, 1921, **172**, 1105—1107. Compare this vol., ii, 110, 257).—Tellurium tetraiodide may readily be prepared in a pure state by heating finely powdered tellurium with an excess of iodine and allowing the mixture to cool slowly. The tetraiodide crystallises out and the excess of iodine may be extracted with carbon tetrachloride. If a further purification is desired, the product is heated in a sealed tube for several hours at 150—160°. So prepared, tellurium tetraiodide has m. p. 280°; D^{15} 5·05. Above 100°, it readily dissociates into tellurium and iodine. The tetraiodide serves as a useful starting material for the preparation of numerous derivatives of tellurium. W. G.

Graphitic Acid—a Colloidal Oxide of Carbon. GEO. A. HULETT and O. A. NELSON (*Trans. Amer. Electrochem. Soc.*, 1920, **37**, 425—439. Compare A., 1916, ii, 31).—The flakes of graphitic acid are shown by the use of polarised light to have a colloidal structure; this view is supported by the fact that the vapour pressure curves of graphitic acid are continuous. It is suggested that the substance is a solid oxide of carbon, having the probable formula C_3O or $C_{11}O_4$. CHEMICAL ABSTRACTS.

Silicon Hydrides. X. Compounds containing Nitrogen. ALFRED STOCK and KARL SOMIESKI (*Ber.*, 1921, **54**, [*B*], 740—758). —Chlorosilane and ammonia react in the gaseous phase at the

ordinary temperature with formation of ammonium chloride, the change occurring most simply in the presence of excess of the former and leading to the quantitative production of *trimonosilylamine*, $N(SiH_3)_3$, m. p. $-105{\cdot}6°$, $D^{-106°}$ 0·895, b. p. 52°, tensions 0·1 mm. −80°; 0·5 mm. −70°; 1·0 mm. −65°; 2 mm. −60°; 3 mm. −55°; 5 mm. −50°; 7 mm. −45·0°; 10 mm. −40°; 14 mm. −35·0°; 21 mm. −29·4°; 29 mm. −24·4°; 38 mm. −20·4°; 52 mm. −14·4°; 65 mm. −11·0°; 89 mm. −4·2°; 109 mm. 0°; 137 mm. +5·0°; 172 mm. 10°; 212 mm. 15·0°. It is a spontaneously inflammable liquid which is stable in the absence of air, and is vigorously decomposed by water, $N(SiH_3)_3+6H_2O=3SiO_2+NH_3+9H_2$. Its vapour density corresponds with the simple formula, $N(SiH_3)_3$. It does not combine with hydrogen chloride or monochlorosilane.

A homogeneous substance could not be isolated from the product of the action of monochlorosilane and an excess of ammonia. The chlorine is immediately converted into ammonium chloride, whilst the silicon remains primarily in the form of volatile compounds in the gaseous phase. The initial product is chiefly *dimonosilylamine*, $NH(SiH_3)_2$, probably admixed with the corresponding tri- and monoamines. The diamine is only comparatively stable in the dilute gaseous condition, and decomposes gradually according to the equation $NH(SiH_3)_2=SiH_4+SiH_2{:}NH$. The latter cannot exist in the unimolecular form, and condenses rapidly to the solid polymeride, $(SiH_2{:}NH)_x$. To a smaller extent, evolution of ammonia occurs in accordance with the scheme:

$$SiH_3{\cdot}NH_2 \longrightarrow NH(SiH_3)_2 \longrightarrow N(SiH_3)_3.$$

The composition of the final residue corresponds with that of a mixture of $(SiH_2{:}NH)_x$ and $N(SiH_3)_3$.

Dichlorosilane reacts with an excess of ammonia at the ordinary temperature in accordance with the scheme $SiH_2Cl_2+3NH_3=2NH_4Cl+SiH_2{:}NH$. Since the latter compound polymerises immediately, only the excess of ammonia remains in the gaseous phase. Reaction does not proceed quantitatively, which is probably explained to a great extent by the fact that the products separate in the solid condition and the intermediate substances thus become covered by layers of material which shield them from the further action of the ammonia. The *polymeride*, $(SiH_2{:}NH)_x$, is a white substance resembling silicic acid. The value of x is certainly very considerable, since examination of the compound produced in benzene solution showed $x=7$—8; the residue obtained by evaporation of the solvent was, however, a viscous liquid which only slowly passed into the solid, doubtless more highly polymerised, condition. The polymeride is decomposed by sodium hydroxide solution, $SiH_2{:}NH+2H_2O=SiO_2+2H_2+NH_3$, the same change being more slowly brought about by water.

In general, the compounds containing nitrogen exhibit a close analogy to the corresponding substances containing oxygen. Thus, the conversion of $NH_2{\cdot}SiH_3$ into $NH(SiH_3)_2$ in the presence of an excess of ammonia is paralleled by the formation of $O(SiH_3)_2$, and not $SiH_3{\cdot}OH$ by the action of an excess of water on monochlorosilane; the conversion of the volatile unimolecular SiH_2O

into $(SiH_2O)_x$ is similar to that of $SiH_2:NH$ into $(SiH_2:NH)_x$, and affords a further example of the remarkable tendency towards polymerisation of substances which contain but few hydrogen atoms directly united to silicon.

The behaviour towards gaseous hydrogen chloride is remarkable; mono-, di-, and tri-silylamines are smoothly and quantitatively transformed into monochlorosilane and ammonium chloride. With the solid polymeride, $(SiH_2:NH)_x$, the action, $SiH_2:NH+3HCl+SiH_2Cl_2+NH_4Cl$, occurs more slowly and passes through several intermediate phases. The ready replaceability of the Si-N group by Si-halogen appears to be quite general with silicon compounds.

H. W.

The Solubility of Different Potassium Salts in Mixtures of Water and Alcohol. M. PIERRAT (*Compt. rend.*, 1921, **172**, 1041—1043).—The solubility in aqueous alcohol of varying strengths at 14° and the electrical conductivity of solutions containing the same weight of salt in the same volume of water have been determined for potassium hydrogen tartrate, potassium perchlorate, potassium platinichloride, potassium silicofluoride, and potassium cobaltinitrite.

W. G.

Decomposition of Sodium, Potassium, Ammonium, and Aniline Hydrogen Sulphates and Potassium Binoxalate and Tetraoxalate by Solvents. TH. SABALITSCHKA (*Ber. Deut. pharm. Ges.*, 1921, **31**, 183—198).—The crystallisation of aqueous solutions of potassium, sodium, ammonium, or aniline hydrogen sulphates results in the formation to a greater or lesser degree of the normal salt and the free acid. Thus pure potassium sulphate was deposited from a solution of pure potassium hydrogen sulphate, whilst a mixture of the normal and acid salts was obtained in the other cases. The addition of alcohol to an aqueous solution of sodium hydrogen sulphate caused the precipitation of the pure normal salt. The precipitate obtained in a similar way with ammonium hydrogen sulphate solutions contained 60—70% of the normal salt. The prolonged extraction of the dry hydrogen sulphates with alcohol in a Soxhlet apparatus likewise resulted in the removal of an excess quantity of the acid, leaving a residue of the normal sulphates in the case of the potassium and sodium salts, and a mixture in the case of the ammonium and aniline salts. The extraction of potassium tetraoxalate with ether and alcohol resulted in a similar decomposition into free acid and a residue of binoxalate, the latter being unchanged by the further action of the solvents.

G. F. M.

Dissolved Gases in Glass. EDWARD W. WASHBURN, FRANK F. FOOTITT, and ELMER N. BUNTING (*Univ. Ill. Bull.* 18, 1920).—All varieties of glass contain dissolved gases which are evolved, with great effervescence and expansion of the glass, when the latter is heated at atmospheric pressure in a vacuum furnace and then suddenly connected to a large vacuum chamber. The amount and composition of the dissolved gas varies with the type of glass and conditions of manufacture. In three types of glass examined the

gases at *N.T.P.* measured 0·2 to 2·0 times the volume of the glass itself. Carbon dioxide, oxygen, and nitrogen (in varying amounts) were the chief constituents. The apparatus used is fully described and illustrated. [See also *J. Soc. Chem. Ind.*, 1921, June.]

A. B. S.

Positive-ray Analysis of Magnesium. A. J. DEMPSTER (*Science*, 1920, **52**, 559. Compare *Physical Rev.*, 1918, **11**, 316).—When a magnesium anode is heated to vaporise it slightly, three isotopes of atomic weight respectively 24, 25, and 26 appear in amounts proportionally 6 : 1 : 1, giving an average atomic weight of 24·375 as compared with the chemically determined value, 24·36.

CHEMICAL ABSTRACTS.

Electromotive Behaviour of Magnesium. I. A. SMITS and R. PH. BECK (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 975—976).—As a preliminary to the investigation of the electromotive behaviour of magnesium and magnesium mercury alloys, which on the whole resemble aluminium and the aluminium mercury alloys in this respect (compare A., 1920, ii, 579, this vol., ii, 371), the melting point–composition diagram of alloys of magnesium and mercury has been determined over the whole range of compositions. The diagram indicates the presence of the compounds $MgHg_2$, MgHg, Mg_3Hg_2, Mg_2Hg, Mg_3Hg, and possibly Mg_2Hg_3. In order to ascertain what corrections must be applied in the concentration for the mercury existing in the vapour phase, the vapour tension of the different mixtures up to 50% mercury has been determined using a glass spring indicator. The results, of which no details are given, indicate that up to this concentration the vapour tensions are very small, even at the melting point of the alloy.

J. F. S.

The Theory of Smelting. II. Equilibria between Pairs of Metals and Sulphur. I. The System: Copper–Lead–Sulphur. W. GUERTLER and K. L. MEISSNER (*Metall & Erz*, 1921, **18**, 145—152).—In a former paper it was shown by Guertler (*ibid.*, 1920, **17**, 192) that when sulphur is added to a mixture of copper and lead, cuprous sulphide is first formed, then lead sulphide, and finally cupric sulphide, and these relations were shown on a triangular diagram. In this diagram the ternary system is divided into three partial systems, (*a*) Pb–Cu–Cu_2S; (*b*) Pb–Cu_2S–PbS, and (*c*) Cu_2S–PbS–S. Thermal and microscopic examination has now been made of a number of mixtures corresponding with points in each of these partial systems. Each pair of constituents in the first partial ternary system shows incomplete miscibility, and consequently an area of incomplete miscibility would be expected in the ternary system, with three separate phases. Actually only two layers are formed, the upper consisting essentially of cuprous sulphide, the lower being an emulsion of lead and copper in which the lead shows a pronounced tendency to liquate downwards. Through this emulsion formation, copper and lead can be made practically completely miscible by addition of 1—1·5% of sulphur. Addition of lead to the Cu–Cu_2S system extends the miscibility gap.

In the partial system Pb–Cu_2S–PbS, a miscibility gap extends almost up to the Cu_2S–PbS line. In absence of free lead, that is, on the Cu_2S–PbS line, there is no gap, but eutectic mixtures only are formed. In the third partial system, Cu_2S–PbS–S, it was expected that the line PbS–CuS would correspond with a quasi-binary series of mixtures, but, owing to the dissociation of cupric sulphide into cuprous sulphide and sulphur on melting, equilibrium was established between lead sulphide, cuprous sulphide, and an apparently ternary crystalline phase. Mixtures richer in sulphur were not further investigated. E. H. R.

Possibility of Separating Mercury into its Isotopic Forms by Centrifuging. J. H. J. POOLE (*Phil. Mag.*, 1921, [vi], **41**, 818—822).—In a centrifuge running at 60,000 revolutions per minute a difference of density of mercury of $1\frac{1}{2}$ parts per 1000, due to separation of the isotopes, should be produced. With liquid neon, a difference of 10% should be obtained. J. R. P.

The Physical Properties of Mercury. ALFRED SCHULZE (*Zeitsch. Metallkunde*, 1921, **13**, 105—113, 139—148).—A review of the literature dealing with the determination of the magnitudes of the physical properties of mercury, grouped under the headings mechanical, thermal, electrical and magnetic, and optical.
E. H. R.

Action of Sodium Sulphide on Ferric Oxide. J. C. WITT (*J. Amer. Chem. Soc.*, 1921, **43**, 734—740).—When ferric oxide is treated with an excess of sodium sulphide, a black, amorphous substance is formed. On removing most of the remaining sodium sulphide and adding water, a brilliant green solution is produced. The results obtained on studying the solution indicate that the colour is due to a colloid and not to a true solution of some iron compound. The exact composition of the disperse phase has not been determined, but apparently it contains neither sulphur nor sodium in chemical combination. The colloid is reversible. It is precipitated by a relatively large amount of sodium sulphide, and is regenerated when the precipitating agent is removed. Sodium sulphide acts also as a protecting agent. The sol can only exist in the presence of a small amount of the sulphide. When the last trace is removed, either by dialysis or by oxidation, the colloid is precipitated. By drawing air through the sol until the sulphide is oxidised to sulphate a new sol is prepared. This is brown in colour and apparently consists of colloidal hydrated ferric oxide. The iron compound is eventually precipitated, although it may remain colloidal for a long time. The green sol contains less than 0·07 gram of iron per litre, and cannot be dialysed in the presence of air. It is therefore exceedingly difficult to determine the exact composition of the disperse phase. J. F. S.

The Constitution of Smalt. A. DUBOIN (*Compt. rend.*, 1921, **172**, 972—974).—Using the method previously described (A., 1892, 1161, 1286), the author has produced deep blue cobalt compounds

similar to smalt. The first had the composition $K_2O,CoO,3SiO_2$ and the second the composition $KCl,K_2O,CoO,4SiO_2$. W. G.

The Introduction of Silicic Acid into the Nucleus of Complex Compounds. ROBERT SCHWARZ and HANS BAUSCH (*Ber.*, 1921, **54**, [*B*], 802—813).—The idea has been occasionally expressed that silicic acid is present in natural minerals, particularly those containing aluminium, in the complex form rather than as the simple silicate, but very little experimental evidence on the point has been brought forward. It is now shown, however, that silica very readily enters the cobaltammine complex, thus supporting the possibility of the hypothesis mentioned above.

Chloropentamminocobalt chloride and hexamminecobalt chloride react smoothly and without formation of by-products when mixed with solutions of homogeneous, crystalline sodium silicate in perfectly definite proportions and concentrations of solution. With the first-named, *chlorotriamminotetrasilicatocobalt*,

$$\begin{matrix}\mathrm{Cl}\\(\mathrm{H_3N})_3\end{matrix}\!\!\geqslant\mathrm{Co}<\!\big\}\mathrm{Si_4O_9},$$

is formed as a reddish-violet, neutral precipitate which when moist has plastic properties resembling clay. Under the microscope, it appears to be non-crystalline. It decomposes above 120°, with the formation of cobalt tetrasilicate: $[Co(NH_3)_3ClSi_4O_9]=CoSi_4O_9+3NH_3+Cl$. It is stable towards water or cold, dilute hydrochloric acid, but is decomposed by the latter in boiling solution with quantitative separation of silicic acid. It is also decomposed by hot, concentrated sodium hydroxide solution. Under similar conditions, hexamminecobalt chloride give a mixture of *silicatotetramminecobalt chloride*, $[Co(NH_3)_4Si_4O_9]Cl$, and *silicatotetramminecobalt silicate*, $[Co(NH_3)_4Si_3O_7]_2SiO_3$. The former is most conveniently prepared by the use of a large excess of the *luteo*-chloride and forms a yellowish-orange precipitate, very sparingly soluble in water. It is readily decomposed by dilute mineral acids, or even by acetic acid, with complete elimination of silica and in this respect resembles the carbonato-complex salts. It decomposes when heated, with production of cobalt tetrasilicate. The latter is obtained when a relatively large excess of sodium silicate is employed, and is of particular interest, since it represents the first synthetic silicato-silicate. It is a yellow powder. The analytical separation of the nuclear and acid silicic acid has not yet been accomplished and the distribution therefore appears at first sight to be arbitrary, but is justified by the behaviour of the two compounds described previously, in each of which the silicic acid accumulates in the nucleus and by the observation that simple metasilicates are invariably formed by the action of sodium metasilicate on metallic salts unless complex formation occurs. The behaviour towards heat also differs from that of the above compounds, which yield pure cobalt tetrasilicate, whilst this one gives a non-homogeneous, greyish-blue product.

The tendency of silicic acid to form complex compounds is particularly shown by the formation of the *substance* $[Co(NH_3)_4Si_4O_9]OH$, a

dull orange-yellow precipitate, instead of the silicate, $[Co(NH_3)_6]_2SiO_3$, by the action of the free *luteo*-base with dioxodisiloxane.

The requisite pure sodium silicate is prepared by fusing the calculated quantities of sodium carbonate and powdered quartz in a platinum crucible at 1100° and allowing the product to cool very slowly. H. W.

Action of Sodium Carbonate on Chrome Alum Solutions. L. MEUNIER (*J. Soc. Leather Trades Chem.*, 1921, **5**, 103—111).—Chrome alum solutions undergo hydrolysis and the basic chromic salts so formed polymerise under the action of heat and more slowly on keeping. The neutralisation of the sulphuric acid formed by hydrolysis by the sodium carbonate, is accompanied by the liberation of carbon dioxide, and this is expelled from the solution by increase of temperature or agitation. The degree of ionisation of the carbon dioxide is influenced by the liquor in which it is produced. Precipitation is due to the sodium carbonate acting as a neutralising agent and also as a coagulating agent on the colloidal solutions of the chromium hydroxide or the polymerised basic chromium salts. D. W.

The Tempering of Brasses containing Tin. LÉON GUILLET (*Compt. rend.*, 1921, **172**, 1038—1041).—The special constituent which occurs in brasses with tin, when the percentage of tin is sufficiently high, has the effect, when the tempering is such that this constituent goes into solution, of considerably improving the mechanical properties of the alloy. Thermal anomalies appear with the special constituent, which possesses the same transformation as the δ-constituent of bronzes. This constituent dissolves at 350° in the β-constituent of brasses. If the alloy contains lead, this does not disappear in the tempering. Tempering at 600° considerably improves alloys containing this constituent, there being a marked increase in the breaking strain, the resilience, and the hardness. W. G.

Revision of the Atomic Weight of Antimony. Analysis of Antimony Bromide. H. H. WILLARD and R. K. MCALPINE (*J. Amer. Chem. Soc.*, 1921, **43**, 797—818).—In an all-glass apparatus, three preparations of antimony were combined with bromine, the resulting product was twice distilled under a pressure of 5—10 mm. as long as gaseous materials could be removed, and then distilled a third time under a pressure of less than 1 mm. into a series of small bulbs which were sealed off as filled. From the time the pure dry materials were placed in the apparatus until the bulbs were broken under tartaric acid only inert gases came into contact with the preparation. The resulting product was analysed for bromine in two ways: first by finding the amount of silver equivalent to the sample in the usual way; secondly, by adding excess of silver nitrate, filtering, and weighing the silver bromide. The precautions taken and the corrections applied include all those described within recent years for similar work. In eleven analyses a total of 46·76580 grams of antimony bromide required 41·86463 grams of silver and formed 72·88245 grams of silver bromide. The ratios are 1·117074

and 0·641611, from which the respective values for the atomic weight of antimony would be 121·799 and 121·755. If for the ratio $SbCl_3 : 3AgBr$, three samples are omitted, because in these cases the fused silver bromide did not give a clear mass, the weights would be 35·69757 of antimony bromide to 55·63121 of silver bromide corresponding with an atomic weight of 121·767. The ratios of silver to silver bromide are 0·574413 and 0·574427, according to whether the imperfect silver bromide determinations are included or omitted. Baxter's determinations of this ratio gave 0·57445. Averaging the volumetric results for the eleven samples with the gravimetric results for eight samples, the most probable atomic weight for antimony becomes 121·773 (Ag=107·880). J. F. S.

Structure of Gold Amalgams as determined by Metallographic Methods. S. A. Braley and R. F. Schneider (*J. Amer. Chem. Soc.*, 1921, **43**, 740—746).—Freezing point–composition curves have been constructed for gold amalgams of compositions varying between 8% and 95% of mercury and a phase diagram has been produced. It is found that in the system gold–mercury there are two eutectics and three compounds, namely, Au_2Hg; Au_2Hg_3; and $AuHg_4$. The compound Au_2Hg freezes at 490°, and forms a eutectic with the solid solution which freezes at 390°. The eutectic has the composition 25 atomic% mercury. The compound Au_2Hg_5 does not form a true eutectic with the compound Au_2Hg. The compound $AuHg_4$ forms a concealed maximum at 100°. This concealed maximum is a break in the curve which is due to the decomposition of the compound $AuHg_4$ at its melting point into Au_2Hg_5 and Hg. This compound forms a eutectic at −41° with the solution of gold in mercury. J. F. S.

Mineralogical Chemistry.

Cesarolite, a New Mineral. H. BUTTGENBACH and C. GILLET (*Ann. Soc. Géol. Belg.*, 1920, **43**, *Bull.*, 239—241).—Small globules aggregated as friable, spongy masses of a steel-grey colour and resembling coke in appearance occur in cavities in galena from Tunis. D 5·29. The mineral is soluble in hydrochloric acid with evolution of chlorine. Analysis gave :

Pb.	MnO.	H_2O	O.	Fe.	Al.	Other metals.	Na_2O.	Insol.	Total.
36·29	42·65	3·30	13·26	0·49	0·79	0·36	0·18	0·75	98·07

Nitric acid extracts only a small part of the manganese (MnO 3·35%), and assuming this to be present as hausmannite the formula is deduced as $PbO,3MnO_2,H_2O$. This is a salt of the acid $H_4Mn_3O_8$, analogous to romanechite. L. J. S.

Minerals from the Limestone Quarries of Pargas, Finland. AARNE LAITAKARI (*Bull. Comm. Géol. Finlande*, 1921, no. 54, 1—114).—A detailed account is given of several crystallised minerals,

occurring in crystalline limestone, for which this locality is famous. Analyses are given of the following: Oligoclase as colourless, tabular crystals; the optical extinctions and *D* correspond with the composition $Ab_{70}An_{30}$; anal. I by P. ESKOLA. Diopside as black crystals; anal. II corresponds with 86% of the molecule $Ca(Mg,Fe)Si_2O_6$; the optical constants are given. Amphibole (var. pargasite), anal. III—V of crystals of three types, III and IV black and V green: the optical constants are given for each and plotted against the composition. The formulæ hitherto proposed for amphibole are

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	F.	Total.	Sp. gr.
I..	59·57	—	25·65	0·27	—	6·51	—	1·34	6·47	—	—	99·81	2·653
II..	49·70	0·43	1·73	4·76	10·61	22·67	9·61	0·19	0·43	0·13	—	100·06	3·42
III..	42·05	0·91	12·60	1·60	11·51	11·85	13·48	1·90	1·97	0·48	1·82	99·41	3·189
IV..	43·90	0·70	12·52	0·38	5·95	12·69	18·91	1·30	1·34	0·61	2·29	99·63	3·186
V..	48·10	0·10	11·05	0·67	1·65	12·50	20·60	1·24	2·54	0·82	1·90	100·37	3·069
VI..	17·6	—	39·6	trace	—	13·0	21·6	—	—	8·1	—	99·9	3·093

discussed, and none of them found to agree closely with the new analyses; possibly certain constituents are present in solid solution. Material heated for two hours at 1000° (*i. e.*, about 100° below the melting point) lost 0·30%, but suffered no essential change in its optical characters. Clintonite (A. Laitakari, *Teknikern, Helsingfors*, 1918, 13) occurs as colourless to pale-green mica-like crystals; anal. VI. Massive löllingite gave on analysis by E. INGMAN:

As.	S.	Fe.	Co.	Ni.	SiO_2.	Total.	Sp. gr.
63·08	3·42	28·95	1·22	0·29	0·45	97·41	7·275

Partial analyses are also given of garnet and apatite.

L. J. S.

Augite from Nishigatake, Japan. RYŌICHI ŌHASHI (*Min. Mag.*, 1921, **19**, 173—180).—A detailed crystallographic and optical description is given of olive-green to black crystals of augite found loose in decomposed basalt. Analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO	Total.	Sp. gr.
51·37	0·58	5·24	2·02	2·96	21·58	16·94	100·69	3·338

corresponding with 74·6% of the diopside molecule, $CaMgSi_2O_6$.

L. J. S.

Formation and Constitution of Kaolin. VICTOR J. BERNAOLA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 392—400).—A theoretical discussion of the mode of formation of kaolin and the supposed occurrence of crystalline particles associated with it. Assuming kaolin to be formed by the removal of sodium, potassium, or calcium silicates from felspars by solution, the formation of crystals is excluded and the crystalline forms observed are merely pseudomorphs after felspars. The porous character of kaolin particles implied by its origin as a metasomatic product from felspars would account for the plastic properties of clays. G. W. R.

The Meteorites of Mount Ayliff, Simondium, Adare, and Ensisheim. G. T. PRIOR (*Min. Mag.*, 1921, **19**, 163—172).—The meteoric iron of Mount Ayliff, Griqualand East, South Africa, was found some time previous to 1907 and weighed about 30 lb. Etched

surfaces show it to have the structure of a coarse octahedrite. Analysis of a portion free from inclusions of graphite and troilite gave :

Fe.	Ni.	Co.	S.	P.	C.	Total.
91·73	6·59	0·69	0·12	0·12	0·51	99·76

Another specimen of the Simondium, Cape Colony, meteorite (A., 1910, ii, 315; 1918, ii, 326) showed on polished surfaces residual grains of unoxidised metal, analysis of which yielded: Ni, 23·79; silicates, 5·67; Fe(+Co) by diff., 70·54. This meteorite is thus rich in nickel, with Fe : Ni about 3; it is still classed with the mesosiderites.

With the idea of testing the theory (A., 1916, ii, 633) that the ratio of MgO : FeO in the ferromagnesian silicates of meteorites varies directly with the ratio of Fe : Ni in the nickel-iron, the following new analyses were made of two meteorites, one (Adare, Co. Limerick; fell Sept. 10, 1813) containing a large amount of iron poor in nickel, and the other (Ensisheim, Alsace; fell Nov. 16, 1492) a small amount very rich in nickel. From detailed analyses of the portions attracted and unattracted by a magnet and of the silicate portions soluble and insoluble in hydrochloric acid, the bulk-analyses are deduced, I for Adare, II for Ensisheim.

	Nickel-iron.			Troilite.					
	Fe.	Ni.	Co.	Fe.	S.	SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.
I	16·81	1·51	0·12	3·57	2·03	36·88	1·50	0·59	9·94
I	2·51	0·72	0·06	4·18	2·41	40·00	1·90	0·34	18·05
	MnO.	NiO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	P_2O_5.	Total.
I	0·15	0·19	1·86	23·32	0·95	0·14	0·68	0·27	100·51
II	0·30	0·46	2·04	25·14	0·94	0·12	0·27	0·26	99·70

The corresponding mineralogical composition is for I: felspar, 7·52; chromite, 0·87; apatite (merrillite ?), 0·63; bronzite (in which MgO : FeO=about 5), 33·83; olivine (MgO : FeO=about 4), 32·64; nickel-iron (Fe : Ni=11), 18·46; troilite, 5·60%; and for II: felspar, 9·32; chromite, 0·51; apatite (merrillite ?), 0·59; hypersthene (MgO : FeO=3), 23·64; olivine (MgO : FeO=2½), 55·03; nickel-iron (Fe : Ni=3½), 3·29; troilite, 6·59%. L. J. S.

Meteoric Stone of Crumlin, Co. Antrim. Sir Lazarus Fletcher, with analysis by G. T. Prior (*Min. Mag.*, 1921, **19**, 149—162).—This stone weighing 4239 grams, D 3·553, was seen to fall on September 13, 1902, at Crosshill near Crumlin. A detailed account is given of the circumstances of the fall. Analysis I (by L. F.) of the silicate portion soluble in hydrochloric acid corresponds with an olivine $3Mg_2SiO_4Fe_2SiO_4$. The bulk-analysis II (by G. T. P.) gives the mineralogical composition : felspar, 10·38; chromite, 0·87; ilmenite ? ($FeTiO_3$), 0·32; apatite ?, 0·59; pyroxene (in which MgO : Fe=about 5), 30·15; olivine (MgO : FeO=3), 43·67; nickel-iron (Fe : Ni=about 7), 8·98; troilite, 5·25%.

	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
I	39·39	—	0·20	—	21·32	0·33	1·43	37·05	199·72
II	40·73	0·17	2·14	0·60	13·24	0·27	2·04	25·36	—

				Nickel-iron.			Troilite.		
	Na_2O.	K_2O.	P_2O_5	Fe.	Ni.	Co.	Fe.	S.	Total.
II	1·07	0·11	0·26	7·75	1·15	0·08	3·34	1·91	100·22

Microscopical examination of thin sections shows that the stone may be classed as a grey hypersthene- (to bronzite-) chondrite.

L. J. S.

Analytical Chemistry.

The Importance of Adsorption in Analytical Chemistry. IX. Glasswool as a Filter Material. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 463—471).—Water and alkali attack glasswool slowly, hydrochloric acid more quickly, the effect increasing with the concentration of the acid. At the ordinary temperature, salts of metals and of the alkaloids are taken up very slowly, but at higher temperatures the speed is greatly increased. The effects appear to be due to the alkaline character of the glasswool, and are independent of the concentration of the salts, so that for very dilute solutions the loss may become relatively very great, especially where warm solutions are filtered through the material.

S. I. L.

Guanidine Carbonate as a Standard Alkali. A. H. DODD (*J. Soc. Chem. Ind.*, 1921, **40**, 89—90T).—Guanidine carbonate, prepared from dicyanodiamide, is readily obtained in a pure state by precipitating it from its aqueous solution with alcohol; it is non-hygroscopic, and the author recommends it for use in standardising acid solutions.

W. P. S.

Colorimetric Estimation of Hydrogen-ion Concentration of Small Amounts of Fluid. LLOYD D. FELTON (*J. Biol. Chem.*, 1921, **46**, 299—305).—One drop of the fluid is mixed on a porcelain plate with one drop of an indicator solution, and the colour is compared with that of similar mixtures made from buffer solutions of known P_H. In order to get approximate results rapidly over a fairly wide range, Clark and Lubs's indicators were employed, mixed in pairs; for instance, thymol-blue and bromophenol-blue for P_H 1·2—4·6 and methyl-red and bromothymol-blue for P_H 4·6—7·6.

G. B.

Estimation of the Hydrogen-ion Concentration of Potable Water. I. M. KOLTHOFF (*Zeitsch. Nahr.-Genussm.*, 1921, **41**, 112—122).—A method is described in which the hydrogen-ion concentration is estimated colorimetrically, using Neutral-red as the indicator, comparison being made with acid and alkaline solutions of the same indicator contained in graduated wedge-shaped tubes and standardised previously against a buffer mixture of known hydrogen-ion concentration. The total carbon dioxide content of the water may be calculated from the hydrogen-ion concentration and the hydrogen carbonate content.

W. P. S.

Detection of Hydrochloric Acid in the Presence of Hydrobromic Acid and Hydriodic Acid. G. G. LONGINESCU and GABRIELA CHABORSKI (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 122—124).—A small quantity of the dry mixed salts is heated in a test-tube with a mixture of two parts of ethyl alcohol and one part of concentrated sulphuric acid, a funnel containing a filter-paper moistened with silver nitrate solution being placed in an inverted position over the mouth of the test-tube. The hydrochloric acid evolved is absorbed by the silver nitrate; the hydrobromic acid is decomposed partly and yields ethyl bromide and dibromoethane, whilst the hydriodic acid is decomposed almost completely. The greater part of the iodine remains in the solution, but a small quantity volatilises and is absorbed by the filter-paper, but remains insoluble when the silver chloride is dissolved in ammonia. If the heating is continued after all hydrochloric acid has been expelled, the bromoethanes and iodine are evolved and may be collected by holding a beaker moistened with water over the test-tube; the beaker is then rinsed out and the solution treated with carbon disulphide and chlorine-water. The latter is added until the violet coloration due to the iodine disappears, when the brown coloration of the bromine remains. If nitrates are present in the original mixture, diphenylamine should be added to the sulphuric acid used in the test. W. P. S.

Electrometric Titration of Hypochlorous Acid. W. D. TREADWELL (*Helv. Chim. Acta*, 1921, **4**, 396—405).—The influence of acidity and alkalinity on the titration of hypochlorous acid with arsenious acid and with potassium iodide has been investigated. In either case, electrometric titration furnishes a highly exact and trustworthy indication of the end point. [Compare *J. Soc. Chem. Ind.*, 1921, 387A.] T. H. P.

Iodometric Studies. I. The Estimation of Iodine by Titration with Sodium Thiosulphate. BOHDAN KOHLER (*Chem. Listy*, 1920, **14**, 137—140, 195—199).—In titrating iodine in acid medium with sodium thiosulphate the presence of a large excess of iodine ions may cause an indefinite end point. More than the theoretical amount of the thiosulphate is required because a portion is used up in a secondary reaction with hydriodic acid. To limit the ionic concentration of the iodine the use of potassium thiocyanate instead of potassium iodide is recommended as an aid in dissolving the iodine (see Bruhns, A., 1920, ii, 773). When using this salt, a minimum acidity of $0·5N$ is required. The titration of iodine with sodium thiosulphate produces tetrathionate quantitatively even in very acid solutions ($6N$HCl) if the ionic concentration of the iodine is kept at a minimum. If potassium thiocyanate is used, the titration can be conducted in the presence of air, since the concentration of iodine is so low that the error due to its oxidation may be considered negligible.

CHEMICAL ABSTRACTS.

Estimation of Iodic Acid and Silver by Electrometric Titration. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1921, **43**, 858—866. Compare this vol., ii, 273).—The estimation of iodates and silver by the electrometric method previously described has been investigated. It is shown that iodate may be accurately estimated by reducing it with an excess of a known iodide solution in dilute sulphuric acid and titrating the excess with potassium permanganate electrometrically. Iodide can be titrated directly with iodate in dilute sulphuric acid solution by the electrometric method. Hydrochloric acid may not be substituted for sulphuric acid except within very narrow limits of concentration in the estimation of iodide with either potassium permanganate or iodate. These estimations may be made in the presence of chloride not exceeding about $0{\cdot}1N$ or in the presence of nitric acid of higher concentration if it contains only traces of nitrous acid. Silver may be accurately estimated electrometrically with pure iodide and permanganate solution. Pure silver may be used as a standard in determining the values of both iodide and permanganate.

J. F. S.

Assay of Fluorides. Modification of Starck and Thorin's Method. EDUARDO D. GARCÍA (*Anal. Soc. Quím. Argentina*, 1920, **8**, 321—324).—Starck and Thorin's method (A., 1912, ii, 295) for the estimation of fluorides in aqueous solution is modified, whereby the excess of calcium in the filtrate from the mixed precipitate of calcium oxalate and calcium fluoride is estimated volumetrically. Knowing the amount of calcium required for the calcium oxalate, the amount of calcium fluoride and, hence, the percentage of fluorine in the original solution, is obtained. Insoluble fluorides are first fused with silica and sodium carbonate. After treatment of the mass with water, silica is removed by ammonium carbonate and fluorine estimated as above.

G. W. R.

Nitrogen Titratable by the Kjeldahl Method. W. MESTREZAT and (MLLE) MARTHE PAUL JANET (*Bull. Soc. Chim. Biol.*, 1921, **3**, 105—130).—A review with bibliography. G. B.

Detection of Nitric Acid. G. G. LONGINESCU and GABRIELA CHABORSKI (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 176—178).—The characteristic odour of nitrobenzene is obtained when a nitrate is heated with a few drops of benzene and concentrated sulphuric acid; if bromides or iodides are also present, it is necessary to neutralise the heated mixture with sodium hydroxide before the odour of nitrobenzene can be noticed. W. P. S.

Estimation of Inorganic Phosphate in Urine by Alkalimetric Titration. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, **46**, 285—295).—The author calculates a titration curve for centimolar mono-potassium phosphate (acid or alkali % plotted against P_{H}) and applies this to the determination. A volume of urine containing

2—7 mg. of inorganic phosphorus is precipitated with magnesium citrate and ammonia; the precipitate is collected in a glass tube containing a paper pad, is then dissolved in excess of acid, and titrated with $N/10$-alkali hydroxide and methyl-red until the colour matches that given by a standard acetate mixture.

G. B.

Electrically Heated Arsenic Reduction Tube. K. ZWICKNAGL (*Chem. Zeit.*, 1921, **45**, 418).—The tube is of the usual shape used with the Marsh apparatus, but the portion which is heated is flattened so that the passage for the gases is about 2 mm. wide; the latter are thus brought into closer contact with the heated wall of the tube. The heating is effected by a resistance wire wound round this part of the tube. W. P. S.

Clinical Method for the Quantitative Estimation of Potassium in Small Amounts of Serum. BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1921, **46**, 339—349).—The sodium cobaltinitrite method (A., 1920, ii, 268) can be used directly on undiluted serum without ashing; the precipitate is oxidised with excess of permanganate, excess of sodium oxalate is added, and this is titrated back with permanganate. One c.c. of serum is required; the error does not exceed 5% of the total potassium present; added potassium is recovered quantitatively. G. B.

New Methods for the Estimation of Potassium and Ammonium. O. ARRHENIUS (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1920, **4**, No. 6, 1—5).—Potassium is determined in soil analysis as follows. The material is freed from all metals except sodium and potassium, the solution made up to 15 c.c., acidified with 5 c.c. of glacial acetic acid, and cooled to 0°. Five c.c. of freshly prepared 10% sodium cobaltinitrite solution prepared according to Biilmann's description (A., 1900, ii, 624) are added and the precipitate is allowed to settle in the cold for about twelve hours. Most of the clear solution is decanted off and the precipitate transferred to centrifuge tubes with capillary stems. The last traces of precipitate are washed into the tubes with a little mother-liquor. The tubes are centrifuged until the height of the precipitate in the capillaries becomes constant. The height is read off by a scale on a mirror and compared with standards. The estimation of 0·01—0·02 mg. of potassium in 20 c.c. of solution is possible. The results are not affected by relatively large amounts of sodium salts.

The method of Folin and Macallum (A., 1912, ii, 683) for the estimation of ammonium is not accurate unless a saturated salt solution is used to suspend the soil. A solution of 0·5 gram of sodium sulphate and 2 c.c. of water is prepared in a test-tube. The weighed sample of soil is added and vigorously shaken. One to two c.c. of saturated sodium hydroxide solution are added and a few drops of petroleum. The tube is connected with an absorption flask containing standard acid, and air is aspirated through the solution to carry over the ammonia. A slow stream of air is used at first, but is increased later and continued for fifteen to twenty

minutes. The sample should not contain more than 1 mg. of ammonia. Higher nitrogen compounds are not attacked, but adsorbed ammonia is recovered. J. R. P.

The Estimation of Sodium in Blood. EDWARD A. DOISY and RICHARD D. BELL (*J. Biol. Chem.*, 1921, **45**, 313—323).—The method devised by Ball (Trans., 1910, **97**, 1408) may be modified for work with blood. The modifications are described in detail, and the estimation may be gravimetric, volumetric, or colorimetric. J. C. D.

Water Analysis. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1921, **34**, 143).—Directions are given for the estimation of hardness, and of calcium and magnesium in water. Soap solution for use in the estimation of hardness may be prepared by neutralising palmitic acid or oleic acid with potassium hydroxide, propyl alcohol being used as the solvent. W. P. S.

The Volumetric Estimation of Zinc. I. M. KOLTHOFF and J. C. VAN DIJK (*Pharm. Weekblad*, 1921, **58**, 538—553).—The estimation by titration with acid is simple, but does not give good results, owing to the precipitation of basic salts instead of zinc hydroxide. The estimation may be carried out indirectly by passing hydrogen sulphide into the solution for thirty minutes in presence of ferrous salts, and titrating the liberated acid with borax, but accurate results are obtained only under narrow conditions of concentration of the zinc and iron.

Treadwell's titration with potassium cyanide in presence of ammonium salts gives good results, the ammonium salt apparently causing the zinc cyanide to separate in a colloidal form which dissolves readily in the excess of cyanide. The mercury double thiocyanate method, however, gives the best results, but chlorides must be absent. An excess of the thiocyanate solution, prepared from 1 mol. of mercuric nitrate and 4 mols. of potassium thiocyanate, is added to the zinc solution, the whole made up to a known volume and filtered, and the excess determined in an aliquot part by means of mercuric nitrate in presence of iron alum. If the concentration of the zinc is below $0{\cdot}01N$, the solution must be left a day before filtering. S. I. L.

Separation of the Metals of the Second Group. G. G. LONGINESCU and G. P. THEODORESCU (*Bull. Acad. Sci. Roumaine*, 1920, **6**, 159—164).—The precipitated mixed sulphides are heated with 10% ammonium carbonate solution, which dissolves the arsenic sulphide; the insoluble sulphides are then dissolved in hydrochloric acid with the addition of potassium chlorate, the solution is diluted, and the lead chloride separated by filtration. The filtrate is treated with sodium carbonate, then with sodium hydroxide, heated, and filtered. The insoluble portion contains the mercury, copper, bismuth, and cadmium, whilst the filtrate contains the tin, antimony, and a small quantity of lead. The precipitate is dissolved in hydrochloric acid, and the solution rendered

ammoniacal; mercury and bismuth are precipitated and the copper and cadmium remain in solution, and these four metals may then be separated and identified in the usual way. The filtrate containing the tin, etc., is treated with sulphuric acid to precipitate the lead, and, after the lead sulphate has been separated by filtration, the tin and antimony are identified in the filtrate. W. P. S.

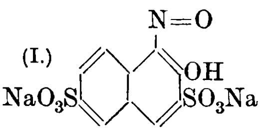
Trihalogen-Methyl Reactions. III. The Use of the Silver Cathode in Electro-deposition of Copper. HOWARD WATERS DOUGHTY and BENJAMIN FREEMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 700—704. Compare A., 1918, i, 57; A., 1919, i, 513).—The authors describe a method for the removal of the copper deposit formed on silver cathodes used in the electro-deposition of this metal. It is shown that an ammoniacal solution of ammonium trichloroacetate dissolves copper, cadmium, and zinc with great ease; it dissolves nickel very slightly, but has no action on silver. In the case of copper, the reaction is strongly exothermic, as is shown by the following example. To a cold solution of 32 grams of trichloroacetic acid in 100 c.c. of ammonia (D 0·90), 19 grams of copper foil were added. The metal was entirely dissolved in six minutes, and the temperature rose from 13° to 105° during the process. The silver electrode is cleaned before use by placing in contact with pure tinfoil in boiling 10% sodium hydroxide solution until quite bright. It is then washed with dilute hydrochloric acid, then with dilute aqueous ammonia, and finally with distilled water. It is rinsed with alcohol, the alcohol ignited, and allowed to burn off. The electrolysis of copper from nitric acid solution is carried out just as is customary when a platinum cathode is used, except that the current must be switched on before the silver cathode is placed in the solution. After the final weighing, the cathode is placed in a wide-mouthed stoppered bottle filled with a 10% solution of trichloroacetic acid in aqueous ammonia (1 part of ammonia D 0·90 and 1 part of water). The copper is removed in about ten minutes, the cathode is then washed and dried as described above. Instead of using trichloroacetic acid, chloroform or carbon tetrachloride may be employed, but in this case the ammonia solution must be made from 1 part of ammonia D 0·90 and 1 part of alcohol. If carbon tetrachloride is used, care must be taken to ascertain that it contains no sulphur compounds. The reaction with both carbon tetrachloride and chloroform is much slower than that with trichloroacetic acid. J. F. S.

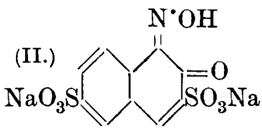
Estimation of Iron by the Cupferron Method. G. E. F. LUNDELL (*J. Amer. Chem. Soc.*, 1921, **43**, 847—851).—The estimation of iron by cupferron has been investigated. It is shown that the precipitation of iron by cupferron is quantitative in hydrochloric or sulphuric acid solutions containing as much as 20% by volume of either acid. The cupferron precipitate of iron is not dissolved by cold dilute hydrochloric acid (1 : 9) wash-water. Ammoniacal wash-waters, which need rarely be employed, may cause losses. These are always indicated by the formation of turbid filtrates. Crystal-clear filtrates and washings are absolutely

essential in accurate estimations of iron by the cupferron method. Cupferron precipitates of iron occasionally exhibit the tendency to creep through the filter. Consequently, when the filtrate or wash-water is even opalescent, the need for such corrective treatments as refiltration or digestion in the cold followed by refiltration is indicated. J. F. S.

Estimation of Iron in Wines. L. MATHIEU (*Ann. Chim. anal.*, 1921, **3**, 106. Compare Malvezin and Rivilland, this vol., ii, 351).—If the ash of the wine is dissolved in 10% sulphuric acid and the solution oxidised by heating with a drop or two of nitric acid, the iron may be estimated colorimetrically by means of potassium thiocyanate. This method is trustworthy and sensitive. W. P. S.

Nitroso-R-Salt. A New Reagent for the Detection of Cobalt. H. S. VAN KLOOSTER (*J. Amer. Chem. Soc.*, 1921, **43**, 746—749).—The methods of preparation and use of a reagent for the detection of cobalt are described. The reagent is prepared by dissolving 35 grams of pure R-salt (sodium β-naphthol-3 : 6-disulphonate) in 400 c.c. of water, acidifying with 10 c.c. of hydrochloric acid (D 1·19), cooling to 8—10°, and running in 7·2 grams of sodium nitrite in 20 c.c. of water drop by drop in the course of thirty minutes. The solution must be continuously stirred, and after a time an orange-yellow precipitate begins to form. The thick paste eventually formed is filtered and the cake obtained worked up with water and again filtered and washed with water and alcohol. The compound is either a nitroso-compound (I) or an oximino-compound (II); it has

(I.)


(II.)


a golden-yellow colour and crystallises from water in fan-shaped crystals. 2·6 Grams dissolve in 100 grams of water at 18°. It is very stable and may be kept indefinitely; its aqueous solution is also quite stable when kept in stoppered bottles. It forms a green compound with ferrous salts, a brownish-yellow compound with nickel salts, and a deep red dye with cobalt salts which has the composition $(C_{10}H_5O_8NS_2Na_2)_3Co$. The formation of this red dye serves as a very sensitive test for cobalt, although the presence of nickel and other metals which form coloured ions affects the sensitiveness, but if the test is conducted as follows 1 part of cobalt in 200 parts of nickel can be detected readily. To 2 c.c. of a dilute solution of the salt to be tested (1·5—2 grams in 100 c.c. of water) is added 1 gram of sodium acetate and 2 c.c. of nitroso-R-salt solution (0·5 gram in 100 c.c. of water). The liquid is boiled over a small flame, and after the gradual addition of 1 c.c. of nitric acid (D 1·4) the boiling is continued for at least one minute. A permanent change in colour toward red indicates the presence of cobalt. The colours produced by the other metals are destroyed by the nitric acid.

It is essential that the original solution should not be acid, for this retards and may prevent the formation of the red coloration.

J. F. S.

Estimation of Tin in Cassiterite. HÉRCULES CORTI (*Anal. Assoc. Quím. Argentina*, 1921, **9**, 44—53).—The method proposed is a modification of that of Fresenius. The material under examination is fused with a mixture of sulphur and sodium carbonate. The fused mass is extracted with water, and stannic sulphide precipitated by dilute hydrochloric acid. The stannic sulphide is dissolved in strong hydrochloric acid and after elimination of hydrogen sulphide, hydrated stannic oxide is precipitated by addition of ammonia solution. This is collected and, after drying and ignition, weighed as stannic oxide. [See further *J. Soc. Chem. Ind.*, 1921, June.]

G. W. R.

The Chemical Examination of Antimony Sulphides. A. VAN ROSSEM and P. DEKKER (*India-rubber J.*, 1920, **60**, 905).—The estimation of free sulphur in antimony sulphides by extraction with organic solvents is impracticable, owing to the instability of the pentasulphide. In the absence of the trisulphide, the reaction $Sb_2S_5+6HCl=2SbCl_3+3H_2S+2S$ is employed, the amount of hydrogen sulphide liberated being a measure of the antimony pentasulphide; the residual sulphur less that produced in the reaction is the free sulphur present in the sulphide. Weber's method of estimation of free sulphur is untrustworthy unless barely ammoniacal solutions are employed. The methods of Weber and Sweet and of Repony for the estimation of moisture and water of crystallisation are revised.

CHEMICAL ABSTRACTS.

Electrolytic Estimation of Gold and its Separation from Copper, Palladium, and Platinum. W. D. TREADWELL (*Helv. Chim. Acta*, 1921, **4**, 364—374).—Gold may be electrolytically deposited, rapidly and quantitatively, from solutions of its chloride containing acetate; this method admits of the separation of gold from copper, palladium, and platinum. The readiness with which palladium is attacked in comparison with platinum when subjected, in hydrochloric acid solution, to anodic polarisation serves as a means for the approximate estimation of the palladium content of a precipitate composed of a large proportion of palladium and of a little platinum.

T. H. P.

Combustions with Tellurium Dioxide. TH. R. GLAUSER (*Zeitsch. angew. Chem.*, 1921, **34**, 154—155; 157—159; 162—163. Compare A., 1914, ii, 216).—A further description of the use of tellurium dioxide in the determination of carbon and nitrogen by combustion. In the case of ferrosilicon, carborundum, etc., the reaction is very slow and for such substances lead oxide, or a mixture of lead oxide and tellurium dioxide, should be used.

W. P. S.

Examination of Urine containing Pentoses. ED. JUSTIN MUELLER (*J. Pharm. Chim.*, 1921, **23**, 317—321).—A urine examined

by the author was optically inactive, but reduced Fehling's solution, and when heated with hydrochloric acid yielded reactions for furfuraldehyde when tested with orcinol or phloroglucinol; pentoses were evidently present. Attention is directed to the fact that the presence of scatole or indoxyl pigments in urine interfere seriously with the above tests for furfuraldehyde. W. P. S.

The Estimation of Blood Sugar. ERIC PONDER and LAURENCE HOWIE (*Biochem. J.*, 1921, **15**, 171—174).—A micro-method for the estimation of sugar in blood is described, which is based on the method of Folin and Wu (A., 1919, ii, 308). The use of the torsion balance is avoided by measurement of the blood in a 0·2 c.c. pipette. C. R. H.

The Iodometric Estimation of Copper and its Use in Sugar Analysis. I. Equilibria in the Reaction between Copper Sulphate and Potassium Iodide. P. A. SHAFFER and A. F. HARTMANN (*J. Biol. Chem.*, 1921, **45**, 349—364).—Both cupric and cuprous salts may be estimated by means of the reversible reaction with iodine $Cu^{++} + 2I^{1} \rightleftharpoons Cu^{+} + I_2$. The position of equilibrium has been determined for the reaction between copper sulphate and potassium iodide at ratios of from 1 to 10 of iodide to 1 of sulphate.

For determination of cupric salts, potassium iodide must be added to give a final concentration of about 0·25 *M*.

For the estimation of cuprous salts, the solution must be so diluted that the final concentration of copper and iodide does not exceed about 5 millemolar proportions each.

The conditions found empirically by Gooch and Heath for cupric salts (A., 1907, ii, 720) and by MacLean (A., 1916, i, 613) and Scales for cuprous salts (A., 1916, ii, 117) comply with these requirements. J. C. D.

The Iodometric Estimation of Copper and its Use in Sugar Analysis. II. Methods for the Determination of Reducing Sugars in Blood, Urine, Milk, and other Solutions. P. A. SHAFFER and A. F. HARTMANN (*J. Biol. Chem.*, 1921, **45**, 365—390).—Methods are outlined whereby the iodometric estimation of cupric or cuprous salts under the conditions laid down in a previous study (see preceding abstract) may be applied to the estimation of sugars in biological fluids. J. C. D.

The Iodometric Estimation of Sugars. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (*Biochem. J.*, 1920, **14**, 754—766).—The authors confirm the opinion of Judd (A., 1920, ii, 395) that the method of Willstätter and Schüdel (A., 1918, ii, 337) gives good results. Certain practical details are given. It is essential that the reacting solutions should be mixed in the order sugar, iodine, alkali. The time required for the oxidation may be reduced to three or five minutes without affecting the accuracy of the method. Normal values were obtained with lactose, which does not support the suggestion of Judd that this sugar is first hydrolysed, and that both the dextrose and galactose molecules

are oxidised. The method was applied to the analysis of the products of the action of diastase on starch, and it was found that iodine does not differentiate between free maltose and that supposed to exist as "maltodextrin." When starch conversion products are fractionated with alcohol, the iodine values agree with the apparent maltose content as found by Fehling's solution.

J. C. D.

Inversion-constants for the Clerget–Herzfeld Method. FR. HERLES (*Z. Zuckerind. Cechoslov.*, 1921, **45**, 223—225).—Herzfeld's well-known formula, giving the inversion-constants for different concentrations of sucrose hydrolysed under the Clerget–Herzfeld conditions, has been confirmed and extended to include corrections for errors arising from the presence of mineral matter in molasses and from the use of basic lead nitrate (Herles's reagent) for clarification. J. H. L.

Estimation of Sucrose by the Inversion Method. V. SÁZAVSKY (*Z. Zuckerind. Cechoslov.*, 1921, **45**, 227—229, 235—238). —Sugar or molasses solutions may be clarified for polarisation and inversion by treatment with a 6% solution of tannin followed, after the liquid has been shaken, by addition of about an equal volume of basic lead acetate solution. The decolorising action, due to the precipitation of lead tannate, is greater than can be attained with basic lead acetate alone, and no error arises from the optical activity of the tannin, as the latter is completely precipitated. The author recommends Stanek's method (A., 1914, ii, 586) of taking the polarimetric readings, before and after inversion, in presence of free citric acid. J. H. L.

New Method for Detecting Lactic Acid in Gastric Juice or Other Organic Fluids. EMILIO PITTARELLI (*Bull. Acad. med.*, 1920, **84**, 132—135).—The test liquid is rendered neutral by addition of a saturated solution of magnesium sulphate, then mixed with permanganate solution, allowed to remain for two to three hours, and filtered. The lactic acid is oxidised to acetaldehyde, which is detected in the filtrate by the development of a red coloration on addition of phenylhydrazine hydrochloride, diazosulphanilic acid, and alkali hydroxide. A sensitiveness of 1 in 70,000 is claimed for the colour reaction. The only substances other than lactic acid likely to be encountered which give the reaction are ethyl alcohol and mannitol. CHEMICAL ABSTRACTS.

Estimation of Ethyl Acetoacetate. HIDEKICHI YANAGISAWA and MASUMI KAMIO (*J. Pharm. Soc. Japan*, 1921, 240—246).—Ethyl acetoacetate (3 mols.) reacts with sodium sulphite, liberating sodium hydroxide (2 mols.). The nature of the reaction is not clear, but it can be utilised for the estimation of the ester: 25 grams of crystallised sodium sulphite are dissolved in water and made up to 100 c.c., 50 c.c. of which are neutralised with *N*-sulphuric acid (say *C* c.c.). Five c.c. of a dilute alcoholic solution of the ester

(about 10%) are shaken vigorously with the remaining 50 c.c. of the sodium sulphite solution and the liberated alkali is titrated with *N*-sulphuric acid (*A* c.c.), using phenolphthalein as indicator. Five c.c. of the 10% solution of the ester are diluted with 20 c.c. of water and any free acid in the sample is titrated with *N*-sodium hydroxide (*B* c.c.). The number of c.c. of *N*-sulphuric acid used for the neutralisation of the liberated alkali would be given by $A+B-C$; 1 c.c. of *N*-sulphuric acid corresponds with 0·1952 gram of pure acetacetic ester. Acetone can also be estimated by the same method. K. K.

Mercurometric Estimation of Oxalic Acid. ARTHUR ABELMANN (*Ber. Deut. pharm. Ges.*, 1921, **31**, 130—131).—To the oxalic acid or oxalate solution in a 100 c.c. flask 30—40 drops of 5*N*-nitric acid and an excess of *N*/10-mercuric nitrate solution, containing sufficient nitric acid to produce a clear solution, are added, followed by about 50 c.c. of saturated chlorine-free potassium nitrate solution and sufficient water to make 100 c.c. After keeping for fifteen minutes, the liquid is filtered and an aliquot portion of the filtrate titrated with *N*/10-ammonium thiocyanate, using ferric ammonium sulphate as indicator. G. F. M.

The Determination of the Acetyl Value of Fatty Substances. ÉMILE ANDRÉ (*Compt. rend.*, 1921, **172**, 984—986).—The saponification value, S, of the fatty substance and the saponification value, S_1, of the same substance after acetylation are determined. Then the acetyl value of the fatty substance is given by

$$S_1-S[1+\lambda S/(1-\lambda S)],$$

where $\lambda=0{\cdot}75$. The value of λ is arrived at by dividing the increase in molecular weight of a monohydric alcohol on acetylation (59—17) by the molecular weight of potassium hydroxide. The acetyl values obtained by this method are always slightly less than those obtained by the method of Lewkowitsch (A., 1890, 72, 91; 1897, ii, 316). W. G.

A New Rapid Method for Detecting Albumoses and Peptones in Urine. EMIL HUGO FITTIPALDI (*Deut. Med. Woch.*, 1920, **47**, 42; from *Chem. Zentr.*, 1921, ii, 478).—A mixture of 2 c.c. of 5% nickel sulphate solution with strong ammonia (D 0·92) is added to 4—5 c.c. of urine made strongly alkaline with potassium hydroxide. In presence of protein, a white or greenish-white ring is formed. An orange-yellow ring is given in the presence of albumoses and peptones. G. W. R.

Use of Edestin in Determining the Proteolytic Activity of Pepsin. J. F. BREWSTER (*J. Biol. Chem.*, 1921, **46**, 119—127).—A modification of the method of Fuld and Levison (A., 1908, ii, 76), together with a method for preparing crystalline edestin from hemp seeds. After mixing various amounts of 1% edestin and 0·1 *N*-hydrochloric acid solutions with equal amounts of 10% sodium chloride in a series of tubes, equal amounts of 1% pepsin are added and the time noted which is necessary to produce a clear solution. G. B.

Iodometric Estimation of the Diastatic Power of Malts. JULIAN L. BAKER and HENRY F. EVERARD HULTON (*Analyst*, 1921, **46**, 90—93).—The maltose formed by the action of malt on starch is oxidised to maltobionic acid by the action of iodine in alkaline solution, the amount of iodine required for the oxidation being a measure of the quantity of maltose present. One, 2, or 3 c.c. of the malt extract are added to 100 c.c. of 2% soluble starch solution, the mixture is kept at 21° for one hour, 10 c.c. of $N/10$-sodium hydroxide are then added, and the whole is diluted to 200 c.c. Fifty c.c. of this solution are treated with 20 c.c. of $N/10$-iodine solution and 30 c.c. of $N/10$-sodium hydroxide solution; after ten minutes, 4 c.c. of $N/1$-sulphuric acid are added and the excess of iodine is titrated with $N/10$-thiosulphate solution. Under these conditions, the diastatic power of the malt equals $16{\cdot}7\,Y/X$, where Y is the number of c.c. of $N/10$-iodine solution used for the oxidation and X the number of c.c. of 5% malt extract taken for the conversion. W. P. S.

Chemistry of Neoarsphenamine [Neosalvarsan] and its Relation to Toxicity. GEORGE W. RAIZISS and M. FALKOV (*J. Biol. Chem.*, 1921, **46**, 209—221).—Analysis of three commercial samples, particularly as regards the distribution of the sulphur. A low arsenic content may be due to the presence of uncombined sodium formaldehyde sulphoxylate, sulphate, or chloride. The arsenic: nitrogen ratio equals the theoretical in good samples, and may be taken as an index of purity. The amount of iodine necessary for complete oxidation is in excess of that required merely by arsenic; this is attributed to uncombined sulphoxylate; sulphoxylate combined with the amino-group does not react with iodine. The amount of combined sulphoxylate indicates that the samples were mixtures of mono- and di-substituted products. G. B.

Examination of Neoarsphenamine [Neosalvarsan]. A. DOUGLAS MACALLUM (*J. Amer. Chem. Soc.*, 1921, **43**, 643—645).—The degree of purity of neoarsphenamine (neosalvarsan) is best estimated by determining the sulphoxylate group ($\cdot CH_2\cdot O\cdot SONa$), as the difference between the total reducing power towards iodine and that due to free reducing substances and arsenic, according to a procedure which is detailed. In the best preparations the ratio sulphoxylate group : arsenic approximates closely to the value 1 : 2, although it is not possible exactly to attain this value.

J. K.

General and Physical Chemistry.

The Variation of the Specific Refraction of Salts dissolved in Dilute Solutions. C. Chéneveau (*Compt. rend.*, 1921, **172**, 1408—1410).—It has been shown previously (A., 1910, ii, 365) that the specific refraction $(n_D-1)/d$, of a dissolved salt is constant for solutions down to a dilution equal to $N/10$. It is now shown that at extreme dilutions the refractive power may diminish or increase, according to the salt used, when the concentration decreases. Results are plotted for magnesium nitrate, potassium chloride, and ammonium nitrate, and it is seen that, in very dilute solutions, the value of $(n_D-1)/d$ decreases with the pressure of the dissolved substance for the two substances first named but increases as the pressure decreases in the case of ammonium nitrate. These results are to some extent in accord with those of Posejpal for gases (*J. Physique*, 1921, [vi], **2**, 85). W. G.

Pole Effect in the Arc Spectrum of Manganese. Sophie Brendel-Wirminghaus (*Zeitsch. wiss. Photochem.*, 1921, **20**, 229—256).—The arc spectrum of manganese has been measured in the ultra-violet over the range $\lambda\lambda$ 3130—3600 and in the greenish-yellow over the range $\lambda\lambda$ 4700—5600 with the object of ascertaining whether manganese exhibits the pole effect which has been observed in the case of calcium. Measurements were made with the light from the positive pole, the negative pole and the centre of the arc. The author is unable to detect any displacement of the lines; the wave-lengths of the lines measured in the three regions are identical within the limits of experimental error. Changing the current from 6 to 10 amperes has no effect on the position of the lines. It is therefore concluded, since the pole effect previously described is only shown by the less well-defined lines, that there is no real displacement of the lines, the effects observed being merely a broadening of unsymmetrical lines. J. F. S.

The Measurement of Rotatory Power in Biaxial Crystals. Louis Longchambon (*Compt. rend.*, 1921, **172**, 1187—1189).—An arrangement of apparatus is described for measuring the rotatory power in biaxial crystals, under conditions approximating as nearly as possible to the theoretical solution of the problem as given by Pocklington (*Phil. Mag.*, 1901, [vi], **2**, 361). In this way, the author has been able to measure the rotatory power of strontium formate, obtaining the value 7° 30′ for a radiation of $\lambda=0{\cdot}579\mu$. W. G.

The *L*-Series of Uranium and the Principle of Combination in *X*-Ray Spectra. A. Dauvillier (*Compt. rend.*, 1921, **172**, 1350—1353).—The L_1 series of uranium photographed alone with very long exposures shows, in addition to the rays l, α_2, α_1, β_6, β_2,

β_7, and β_5, two new satellites of β_2, namely, $\beta'_2=754\cdot1\times10^{-11}$ cm. and $\beta''_2=747\times10^{-11}$ cm. If the L_1 series and its discontinuity of absorption are taken on the same plate, a very clear white ray (absorption ray) appears just beyond the discontinuity and having the same breadth as the emission rays. In the L_2 series only the rays η, β_1, γ_5, γ_1, γ_6, and γ_2 which give the L doublet of Sommerfeld were found. A new line, $\gamma_8=568\cdot9$, was found in the L_3 series, thus giving in this series the rays γ_8, γ_4, γ_3, γ_7, γ_9, β_8, β_9, β_3, and β_4.

W. G.

Magnetic Spectrum of the β-Rays Excited by γ-Rays. C. D. Ellis (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 261—271).—The magnetic spectrum of the β-rays excited by the γ-rays of radium-*B* in uranium, lead, platinum, tungsten, and barium has been measured. It is shown that the main lines are formed by electrons ejected from the *K* ring by definite γ-rays, each type of γ-ray being characterised by a certain energy. The magnetic spectrum of the β-rays of radium-*B* is accounted for on this basis. The magnetic spectrum of the low velocity β-rays of thorium-*D* has been measured and is explained in the same way as the radium-*B* β-ray spectrum. The wave-lengths of the γ-rays of radium-*B* are calculated, on the basis of the quantum theory, from the characteristic energies found. Evidence is adduced to show that the greater the energy of binding of an electron the greater is the probability of it absorbing this hard γ-radiation. J. F. S.

Electron Velocities for the Production of Luminosity in Atmospheric Neon. Frank Horton and Ann Catherine Davies (*Phil. Mag.*, 1921, [vi], **41**, 921—940).—No luminosity is produced in neon as a result of the first type of ionisation, beginning at 16·7 volts. This suggests that the corresponding spectrum may consist entirely of lines outside the visible region. The fact that the combination principle applies without modification between some of the lines excited at 20·0 volts and some at 22·8 volts excludes the possibility that these correspond with two distinct elements. They must correspond with the removal of differently situated electrons from the neon atom, and lines as closely related as those of a principal and the corresponding subordinate series can arise from the return of electrons removed from different positions within the atom.

J. R. P.

Emission of Electrons under the Influence of Chemical Action. O. W. Richardson (*Phil. Trans.*, 1921, [*A*], **222**, 1—43). —The emission of electrons from the liquid alloys NaK_2 and NaK, when acted on by carbonyl chloride, chlorine, hydrogen chloride, and water vapour at very low pressures, was examined, the alloy being dropped through the gas. The current-potential curves resemble those found in thermoionic emission and are not inconsistent with a distribution of energy among the electrons corresponding with that applying to the molecules of a gas, according to Maxwell's law, at a temperature of about 3300° abs. in the case of carbonyl chloride, and about 4900° abs. in the case of chlorine. On

the assumption that the heat of reaction is given to one electron emitted, the energy of the latter would correspond with a temperature about fourteen times that calculated from the curves, which is taken to mean that the energy of reaction is divided among the atoms as well as the electrons. J. R. P.

Electrical Conduction of an Hydrogen Alloy. DONALD P. SMITH (*Proc. Nat. Acad. Sci.*, 1921, **7**, 28—34).—The conductivity of palladium charged with hydrogen has been measured at 25°, using different currents in the measurements. It is shown that the resistance varies with the current employed, and consequently the temporary supplementary conduction exhibited by metals during cathodic occlusion of hydrogen and for some time afterwards, is not to be regarded as metallic conduction. The results are in keeping with the hypothesis that the conduction is effected by a transient form of the occluded hydrogen, probably monatomic, and consists in a transport of electrical charges between points of different potential within the metal. The measuring currents employed in the present work were 4·2 and 2·1 milliampères, and it seems likely, with much larger measuring currents than these, that the supplementary conduction would approach a limiting value, owing to the inability of ordinary diffusion to maintain the concentration of hydrogen atoms in the regions from which these are driven by the current. Above this limit the dependence of resistance on current would not be observed. J. F. S.

Allotropic Varieties of Oxides. (MLLE) S. VEIL (*Compt. rend.*, 1921, **172**, 1405—1407).—The curve showing the variations in the conductivity of magnetic oxide of iron with temperature has a marked double inflexion approximately at the Curie point. This anomaly is only shown with rising temperature. It is possible that this is due to the formation of an allotropic modification of the oxide. The curve for cadmium oxide shows three points of inflexion and on the basis of these results the existence of three allotropic modifications, α, β, and γ, of this oxide is suggested. W. G.

The Limiting Value λ_∞ of Molecular Conductivity in Non-aqueous and Aqueous Solutions. P. WALDEN (*Zeitsch. anorg. Chem.*, 1921, **115**, 49—86).—The calculation of the limiting value of molecular conductivity in aqueous solutions was discussed by Lorenz (A., 1920, ii, 6), who compared the values obtained from the Ostwald-Bredig rule $\lambda_\infty = \lambda_v + d_v$, where d_v is a constant depending only on the dilution, with those obtained by the alternative Kohlrausch formulæ $\lambda_\infty = \lambda_v + a/v^{0 \cdot 5}$ and $\lambda_\infty = \lambda_v + b/v^{0 \cdot 33 \cdots}$. He also showed that, for aqueous solutions of sodium chloride, the best results were given by the formula $\lambda_\infty = \lambda_v + b'/v^{0 \cdot 45}$. The two formulæ containing $v^{0 \cdot 5}$ and $v^{0 \cdot 45}$ respectively have now been tested for non-aqueous solutions at 25°. The data chosen for the comparison included those relating to solutions of the typical binary iodides, sodium, potassium, tetramethyl, tetraethyl- and tetrapropyl-ammonium iodides in the following solvents: formamide,

formic acid, cyanoacetic ester, nitrobenzene, benzonitrile, acetophenone, ethyl alcohol, nitromethane, benzaldehyde, epichlorohydrin, methyl alcohol, acetonitrile, pyridine, propionitrile, and acetone.

From the values of λ_∞ calculated from the $v^{0.45}$ formula, the values of d_v in the equation $\lambda_\infty=\lambda_v+d_v$ were calculated for each solvent for different dilutions, and it was found that the Ostwald-Bredig rule can be applied to all these solvents as well as to water through the range of dilutions from $v=256$ to 50,000. In the above list of solvents, these are placed in ascending order of the d_v values at each dilution, water coming between formic acid and cyanoacetic ester.

From general considerations it was deduced that the product $d_v . \epsilon . \eta_\infty$ should be constant at a particular dilution for all solvents, ϵ being the dielectric constant and η_∞ the internal friction. This deduction proved to be correct, and it was further found that by introducing the dilution factor $v^{0.45}$ an expression was obtained which is general for all solvents and all solutes at all dilutions, namely, $K=d_v . \epsilon . \eta_\infty . v^{0.45}$. The mean value of this constant K for all the above solvents, including water, at all dilutions, was found to be 51·4, the divergences on either side from the mean being remarkably small. It follows that, when the values of ϵ and η_∞ are known for any solvent, d_v can be calculated for any dilution, and from a single observation of λ_v, λ_∞ can be calculated and hence $\alpha=\lambda_v/\lambda_\infty$. The general relation between d_v, ϵ, and η_∞ appears to hold for all temperatures.

It has been shown previously (this vol., ii, 160) that the product $\lambda_\infty \eta_\infty$ is a constant for all ionising solvents, independent of the temperature between 0° and 25°, but depending, within limits, on the nature of the solute. The above general expression can be transposed to the form

$$(1-\alpha)\epsilon . v^{0.45}=51{\cdot}4/\lambda_\infty \eta_\infty=\text{const.}$$

It follows from this that, if the product $\lambda_\infty \eta_\infty$ is known for a salt in any one solvent, its degree of dissociation in any other solvent at any dilution can be calculated.

When the values of d_v are calculated from Kohlrausch's $v^{0.5}$ equation, the value of the constant $K'=d_v . \epsilon . \eta_\infty . v^{0.5}$ is 65·7. The numerical relationships between the values of λ_∞ deduced from the different formulæ have been calculated, and it is shown that $\lambda_\infty[v^{0.45}]=1{\cdot}0077\lambda_\infty[v^{0.5}]$. E. H. R.

A Variable Resistance. O. MAASS and C. H. WRIGHT (*J. Amer. Chem. Soc.*, 1921, **43**, 1179).—A variable resistance which has many advantages over a slide wire is described. The apparatus consists of a platinum wire (1 ohm per 50 cm.) which is held taut down the centre of a vertical glass tube (1—2 cm. diam.); the wire passes out of the tube at either end through cement seals. Near the base of the tube a side tube is sealed on which is connected to the bottom of a bulb of capacity greater than that of the tube. The bulb contains mercury, and as the tube containing the wire

is evacuated, any change of external pressure on the mercury in the bulb varies the height to which the mercury rises in the tube and so vary the resistance. The advantages of the apparatus are (1) the wire is maintained in a vacuum and consequently keeps a constant resistance, and (2) since the resistance is controlled by the applied pressure the resistance readings may be made directly from the pressure readings, which means that an accuracy of 0·002 ohm can readily be obtained. J. F. S.

Determination of the Electrical Resistance of Alloys of Lead–Tin and Lead–Zinc at High Temperatures. SEIBEI KONNO (*Sci. Rep. Tôhoku Imp. Univ.*, 1921, **10**, 57—74).—The electrical resistance of alloys of lead and tin and lead and zinc have been measured over the whole range of concentrations, both during heating and cooling, above and below their melting points. The temperature–resistance curves have been plotted, and from these the equilibrium diagrams of the alloys have been constructed. They are found to coincide almost exactly with those obtained by thermal analysis. The rate of separation of the solid solution during solidification has been calculated both from the resistance–temperature curves and from the equilibrium diagram, and the results obtained in the two cases show a good agreement.
J. F. S.

Apparent Irreversibility of the Calomel Electrode. A. W. LAUBENGAYER (*J. Physical Chem.*, 1921, **25**, 332—336).—It has been shown by Paschen (A., 1890, 552) that a mercury anode polarises more strongly in hydrochloric acid than in sulphuric acid. This point has been investigated, and in preliminary experiments it is found that a mercury anode in hydrochloric acid becomes coated with a black film of an apparently high resistance. The potential drop for various currents has been measured for the following systems: Hg (anode) | NHCl | Pt (cathode); Hg (anode) | Hg_2Cl_2,NHCl | Pt (cathode): Hg (anode) | Hg_2Cl_2,NKCl | Pt (cathode): Pt (anode) | Hg_2Cl_2,NHCl | Pt (cathode); Hg (anode) | NH_2SO_4 | Pt (cathode); Hg (anode) | Hg_2SO_4,NH_2SO_4 | Pt (cathode): Pt (anode) | Hg_2SO_4,NH_2SO_4 | Pt (cathode). The results show that the apparent irreversibility of the calomel electrode is not real, but is due to the formation on the mercury anode of a strongly adsorbed film of mercurous chloride, which offers a high resistance to the passage of the current. If this is scraped off as fast as it is formed it becomes a simple matter to prepare calomel electrolytically at a relatively low voltage. J. F. S.

New Conceptions of Electrolytes. I. The Degree of Dissociation of Acetic Acid in Water and in Salt Solutions. ERLING SCHREINER (*Zeitsch. anorg. Chem.*, 1921, **115**, 181—201).—A theoretical paper in which formulæ are derived for correcting the dissociation constant, as ordinarily determined from conductivity measurements, for the viscosity of the solution, inter-ionic force, and the activity of the water, that is, the hydration of the hydrogen ion. The conductivity of acetic acid as determined by

different observers is thus corrected at 25° over the range of dilution from 0·0005 to 2·6 normal. The law of mass action is shown to hold up to the highest concentration. From potential measurements at 18° and 25° of acetic acid solutions containing sodium acetate or other salts, the activity of the acetate ion and the dissociation constant of acetic acid have been calculated. Such measurements do not, as has been generally supposed, determine the hydrogen-ion concentration, but the activity of the hydrogen ions, which is associated only with the non-hydrated ions. The dissociation constants of acetic acid calculated thus agree well with those calculated from the conductivity measurements. Taking the activity constant of the hydrogen ion as 0·2, that of the acetate ion is the same in sodium acetate solution and 0·3 in sodium and potassium chloride solutions. E. H. R.

New Method of Measuring Electrolytic Conductivity. CHARLES MARIE and W. ALBERT NOYES, JUN. (*J. Amer. Chem. Soc.*, 1921, **43**, 1095—1098).—A new method for measuring the electrical conductivity is described. The method consists in inserting two hydrogen electrodes of exactly equal potential in the solution in question and an ordinary direct current. A Wheatstone bridge is used to determine the resistance. Measurements of the equivalent conductivity of various acids and sodium chloride solutions have been made and negligible differences between the direct current values and the values found by Kohlrausch's method are found except for solutions above 0·5*N*-sulphuric and hydrochloric acid. J. F. S.

Dielectric Constants of Electrolytic Solutions. R. T. LATTEY (*Phil. Mag.*, 1921, [vi], **41**, 829—848).—Formulæ are deduced for the determination of dielectric constants of electrolytes by the condenser method. Anomalous absorption was not formed in the experiments. The circuit consisted of two receiving inductances, two variable condensers in series, and a thermal converter attached to a millivoltmeter. The following dielectric constants were determined:—Water 81·05 at 18°. Glycerol 51·15 (17—18°). Sucrose solutions: 6·84% 81·2 (13°), 11·92% 69·8 (14°), 20·6% 79 (16°). Potassium chloride 0·000755*N* 80·25 (15·4°), and 75·0 (15·4°); 0·00151*N* 77·7 (10·6°); 0·00755*N* 66·25 (16·8°). Cupric sulphate 0·00114*N* 75·2 (15·1°); 0·00228*N* 78·2 (13·2°); 0·00456*N* 73·9 (14·8°). Tetraethylammonium naphthalene-β-sulphonate 0·002*N* 76·3 (16·6°); 0·005*N* 69·0 (14°). The dielectric constant of water is independent of the frequency between wave-lengths of 17 and 52 metres. The electrolytes investigated appear to lower the dielectric constant of water and are analogous to the majority of non-electrolytes. J. R. P.

Electrical Conductivity in Solid Crystallised Compounds II. Transportation and Wandering of Ions in uniform Solid Electrolytes. C. TUBANDT (*Zeitsch. anorg. Chem.*, 1921, **115**, 105—126).—In a former paper (A., 1920, ii, 279) it was shown that the study of the electrolysis of solid crystalline salts was facilitated

by interposing between the cylinder of salt under examination and the platinum cathode a cylinder of cubic silver iodide. By this means, short-circuiting by the growth of a bridge of metal between the electrodes was prevented. The same device has been used in studying ionic migration in the electrolysis of silver bromide and chloride, lead chloride, lead fluoride, silver sulphide, and cuprous sulphide. To determine whether the current is carried by the positive or negative ion or by both, two or more carefully made compressed cylinders of the salt under examination, of known weight, were held by pressure between a silver anode and a platinum cathode, generally with a cylinder of silver iodide interposed between the last cylinder of the salt and the cathode. By weighing the separate cylinders before and after electrolysis, after allowing for the weight of silver taken up at the anode and deposited on the cathode, any transference of the negative element could be detected. With silver iodide, bromide, and chloride it was found that the current was carried entirely by the positive silver ion. In the case of silver iodide the migration velocity of the ion was, at 145°, $0{\cdot}55 \, . \, 10^{-3}$ cm. per sec., about the same value as in aqueous solutions at 18°, whilst at 552° the value was $1{\cdot}1 \, . \, 10^{-3}$. For silver bromide at 422° the velocity was $0{\cdot}15 \, . \, 10^{-3}$ and for silver chloride the highest value, close to the melting point, was $0{\cdot}03 \, . \, 10^{-3}$ cm. per sec. In the case of lead chloride, however, the current was entirely carried by the chlorine ion, the gain in weight of the lead chloride cylinder adjacent to the anode being exactly equivalent to the silver deposited on the cathode in the voltameter which was included in the circuit. In the case of lead fluoride also, the current was conveyed entirely by fluorine ions. Silver sulphide was found to be a true electrolytic conductor above 180°, the silver ions being the carriers with the high migration velocity of 0·11 cm. per sec. Difficulties were encountered in the experiments with cuprous sulphide, but sufficient evidence was obtained to show that the cubic form of this substance is a pure electrolytic conductor, the carriers being the positive cupro-ions. The fact that in some salts only the positive, in others only the negative ions, are mobile, may have a bearing on the lattice structure of these salts. E. H. R.

Activity Coefficient of Strong Electrolytes. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1921, **43**, 1112—1154).—A theoretical paper in which the various methods of determining the exact values of the activity coefficient (thermodynamic degree of dissociation) are discussed. It is shown that the activity coefficients of sodium chloride ($0-6M$), calculated from freezing points, agree with those calculated from electromotive force within a few tenths per cent., notwithstanding the fact that one term alone in the freezing-point equation, which involves the heat of dilution, affects some of the results by 20%. An even more extensive test of the several methods is furnished in the case of sulphuric acid, where satisfactory agreement is obtained over the range $0-20M$ (66% acid) by three different methods. Calculations of activity coefficients in mixtures, especially from the solubility of

salts in the presence of other salts, lead to an extremely useful and general rule based on the new conception of ionic strength. Each ion contributes to this ionic strength by an amount which is proportional to its stoicheiometrical molarity multiplied by the square of its valency. In accordance with this rule, the activity coefficient of every strong electrolyte (and the individual activity of every ion) is the same in all dilute solutions of the same ionic concentration. It therefore depends in no way on the number or the nature of the ions of which the solution is composed. J. F. S.

Constant Volume Explosion Experiments. S. LEES (*Proc. Camb. Phil. Soc.*, 1921, **20**, 285—290).—It has been suggested that the differences between the results for the specific heats of gases obtained by the explosion method and those found by heating at constant pressure might in part be due to the differences in temperature at any instant in different parts of the explosion vessel. These are shown by calculation to correspond with a correction of not more than 1% at 1600°, which is within the limits of experimental error. J. R. P.

The Specific Heat of Technical Copper–Zinc Alloys at Higher Temperatures. FR. DOERINCKEL and MAX WERNER (*Zeitsch. anorg. Chem.*, 1921, **115**, 1—48).—The specific heats of brasses containing 58%, 63%, 67%, 72%, and 85% of copper, and of pure copper, were determined at temperatures between 100° and 800° with the object of determining the influence of composition and of temperature on the specific heat. The water calorimeter method was used, and the determinations were made on both untempered and tempered alloys. In the case of the untempered alloys, when the mean specific heat was plotted against temperature, the curves showed a discontinuity characterised by a sudden rise in the specific heat in the neighbourhood of 470°. This discontinuity was most marked in the low copper alloys, small in the 72% and absent in the 85% copper alloy. In some cases, after tempering at 800°, the specific heat at 500° and 600° was lowered to such an extent that the discontinuity in the curve disappeared. The discontinuity may be due to the transition observed by Carpenter and Edwards at 470° from β-mixed crystals to α- and β-brass, but this explanation is not altogether satisfactory, since this transformation takes place very slowly. Owing to the contradictory character of some of the experimental results on the effect of tempering, it is assumed that the transition may be influenced in an indeterminate manner by small amounts of impurity present in the brass. The specific heat of the alloys increases with increasing content of β-mixed crystals.

The mean specific heat of tempered alloys is expressed by the linear equation $c_m=a+b(T-t)$, and the true specific heat by $c_w=a+2b(T-t)$, where a and b are constants and $t=20°$. For copper, $a=0{\cdot}0922$ and $b=0{\cdot}000011789$. As the proportion of zinc increases, a diminishes and b increases, and for brass containing 57·3% of copper, $a=0{\cdot}0895$ and $b=0{\cdot}00003354$. When the mean or true specific heat is plotted against per cent. copper, at constant

temperature, curves are obtained for each temperature showing the effect of copper concentration on the specific heat. In the α-mixed crystal region the variation of specific heat with copper concentration is practically linear at all temperatures; above 500°, the specific heat increases with decreasing copper concentration, whilst below 300° it decreases. At 65·81% of copper the curve shows a sudden change of direction as the copper concentration falls, the specific heat increasing rapidly at temperatures above 100°, the more rapidly the higher the temperature, and falling at temperatures below 100°. The change of direction of the curve corresponds with the saturation limit for α-mixed crystals at 64% copper. It is noteworthy that at temperatures near 100° there is practically no discontinuity in the specific heat–concentration curve, the specific heat remaining practically constant at all concentrations. By extrapolation of the curves to 53% copper, the saturation limit of β-mixed crystals, the specific heat of β-brass at temperatures from 100° to 800° was calculated. [See also *J. Soc. Chem. Ind.*, 1921, July.] E. H. R.

New Equation of State of Gases, Founded on a Knowledge of the Internal Pressures. A. LEDUC (*Compt. rend.*, 1921, **172**, 1167—1172).—A mathematical paper in which the author deduces the equation $[\pi+\tau/\nu^2(4^{1/\tau}-1)](3\nu-1)=8\tau$, from which it is seen that the interior pressure and the internal pressure tend towards the same limit log $4/N^2$. If this is applied to the calculation of the coefficient of dilatation, β, the value obtained for sulphur dioxide is 389×10^{-5}. W. G.

The Condition Diagram of Carbon. J. A. M. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1921, **115**, 218—224).—A theoretical paper in which the work of Lummer, Fajans (A., 1920, ii, 469), van Laar (this vol., ii, 17) and others on the temperature of the crater of the carbon arc at high and low pressures is discussed. The equation connecting temperature and pressure deduced by van Laar is the most satisfactory, whilst the accuracy of Lummer's observation of the appearance of liquid carbon below 4700° is open to serious doubt. E. H. R.

Comparison of Tammann's and Cuy's Theories of the Periodic Irregularities of Physical Properties in Homologous Series. EUSTACE J. CUY (*Zeitsch. anorg. Chem.*, 1921, **115**, 273—287).—Tammann's theory of the cause of the alternate higher and lower melting points in the successive members of the fatty acid series (A., 1920, ii, 285) is based on the single observation that acetic acid is dimorphous whilst formic acid is not. Many other physical properties show the same kind of alternation in homologous series, and it is shown that generally, when the numerical value of the property is plotted against the number of carbon atoms, the points corresponding with an even number of carbon atoms lie on one smooth curve and those corresponding with an odd number on another. The melting points of the paraffin hydrocarbons are a case in point. Here, although the melting points do not alternately

rise and fall, the melting point differences between successive members of the series are alternately larger and smaller. Other examples of alternation are furnished by the melting points of the glycols and $\alpha\alpha'$-diamines, solubilities in the oxalic acid series, molecular rotations in the amyl esters of normal fatty acids, and boiling points of normal aldehydes, *cyclo*methylenes and acetic esters of normal alcohols. All these phenomena can be explained by Cuy's theory of the alternate positive and negative character of carbon atoms in a normal carbon chain (A., 1920, i, 361). On this theory the addition of one positive or negative carbon atom changes considerably the electronic character of the chain, whilst the addition of two links, one positive and one negative, preserves the general electronic character. Alternation of physical properties in normal chain series is therefore to be expected. E. H. R.

Periodic Irregularities of Physical Properties in Homologous Series. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1921, **115**, 288—289).—A brief reply to Cuy (previous abstract). E. H. R.

Effect of Finely Divided Material on the Freezing Points of Water, Benzene, and Nitrobenzene. F. W. PARKER (*J. Amer. Chem. Soc.*, 1921, **43**, 1011—1018).—The freezing point of water, benzene, and nitrobenzene in the presence of finely divided ferric hydroxide, alumina, silica, and Carrington silt loam has been determined by the method described by Bouyoucos and McCool (A., 1917, i, 510; 1919, i, 115). The results indicate that finely divided material causes a depression of the freezing point of a liquid when the liquid exists in the film or capillary condition in the solid material. The depression of the freezing point due to the solid material and that due to material in solution are additive. The concentration of the soil solution cannot be measured by the freezing-point method except at very high moisture content. The significance of the lowering of the freezing point by finely divided solid material to the behaviour of moist living tissue at low temperatures is indicated. J. F. S.

Freezing Points of Organic Substances. III. JEAN TIMMERMANS (*Bull Soc. chim. Belg.*, 1919, **28**, 392—402. Compare A., 1911, ii, 854; 1914, ii, 168).—Organic compounds obey a law of convergence in that the melting points of the higher terms of all the homologous series tend towards a common limit of 117°. There are, however, certain series which do not obey this law, but they are considered as constituted by substances with particular structures, such as the amino-acids, substances containing two amide groups or an analogous group. It results from the above law that, for the higher members of a series, physical constants such as the melting point are not a criterion for differentiating one homologue from another. W. G.

Freezing Points of Organic Substances. IV. New Experimental Determinations. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1921, **30**, 62—71).—The freezing points of a further 94 specially purified organic liquids were determined (compare

preceding abstract) at temperatures ranging from $-187 \cdot 8°$, the freezing point of propane, upwards. The results are expressed in tabular form in the original paper. G. F. M.

Freezing Points of Organic Substances. V. The Odd and Even Alternation and the Lowest Melting Point in a Homologous Series. JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1921, **30**, 89—97).—A theoretical paper in which the author discusses the relationship between melting points and spatial structure of the molecule. He shows that the linear structure of open carbon chains as postulated by Hinrichs (*Compt. rend.*, 1891, **112**, 998; A., 1891, 1330, 1441) is in accord with the experimental facts as to the melting points of members of homologous series. The alternation of melting points between the odd and even members of a series is a general phenomenon, the odd members melting lower than the even members in series where the molecule is symmetrical in relation to the centre of the chain, for example, the oxalic acid series, paraffins, fatty acids, etc., but this alternation may be inverted in series not having this symmetry, namely, ketonic acids, alkyl chlorides, etc. This alternation may be completely masked by the mass of a characteristic group being so great as to cover the influence of the carbon chain. The existence of a minimum melting point for one of the members of a series other than the first is very general, and is in accord with Hinrich's hypothesis. This minimum may be situated anywhere from C_1 to C_{10}, according to the series, but in the majority of cases it is reached at the C_3 member. G. F. M.

Latent Heats of Vaporisation. ERIC KEIGHTLEY RIDEAL (*Proc. Camb. Phil. Soc.*, 1921, **20**, 291—298).—The latent heats of evaporation of metals are calculated from two formulæ, (1) $L=Nh(v_2-v_1)$, where N is Avogadro's constant, h is Planck's constant, v_2 the vibration frequency of the vapour and v_1 the vibration frequency of the solid or liquid. v_2 is supposed to correspond with a radiation far in the infra-red, since experiment shows that practically all vapour atoms are active, *i. e.* adhere to the solid when they strike it, and the activating energy is therefore small. v_1 should correspond with some line in the spectral series, each representing a different degree of activation. It is shown by calculation that fair agreement is found when a line fairly widely separated from the other lines is chosen; this is at, or near, the head of a series. The second formula supposes that the activation of a metal atom occurs in two stages, the activation of the positive nucleus and the activation of the electron. If the corresponding activation frequencies are v_3 and v_4, respectively, and the activation frequency of the atom, which corresponds with the radiation potential, is v_5, then, according to Haber: (2) $L=\frac{1}{2}Nh\{v_5-(v_3+v_4)\}$. The values of L calculated by the two formulæ agree fairly with the experimental numbers except in the cases of mercury, tin, and lead. The values of v_3 were calculated by Lindemann's formula; those of v_4 by Haber's formula $Mv_3^2=mv_4^2$, where M and m are

the atomic and electronic masses, respectively. Where experimental values of v_5 were not available, they were calculated from the relation $v_5=v_4/2{\cdot}3$. The theory is extended to non-conductors.

J. R. P.

Vapour Tension Tables for Measurement of Temperatures between +25° and −185°. ALFRED STOCK, FRITZ HENNING, and ERNST KUSS (*Ber.*, 1921, **54**, [*B*], 1119—1129).—The tension thermometer consists of a thin glass tube on the end of which a small bulb is blown in which the liquid condenses during measurement; the tube is connected by a glass spring to a bulb of about 50 c.c. capacity (which enlarges the capacity of the instrument and thereby diminishes the error due to the possible presence of traces of gaseous impurity); the bulb is connected with a glass manometer and also a side tube which permits the introduction of the filling material. The apparatus is drawn to scale in the original communication and various modifications are suggested. The apparatus for filling is also figured. The various substances used for filling are as follows: the individual range (within which the tension has been measured for each degree centigrade by comparison with the temperature scale of the hydrogen thermometer of the Physikalisch-technische Reichsanstalt) being indicated in brackets: carbon disulphide (+25 to −18°), sulphur dioxide (−10° to −57°), ammonia (−33° to −77°), carbon dioxide (−77° to −110°), hydrogen chloride (−85° to −111°), phosphine (−87° to −133°), ethylene (−103° to −150°), ethane (−150° to −182°), oxygen (−179° to −185°). The methods of preparation and purification of the substances are fully described.

By means of these tables of tensions, it is readily possible to measure any temperature between the atmospheric and −185° accurately to within 0·1°. The thermometers are easily made and have the great advantage that they are not susceptible to the presence of impurities in the air of the laboratory. They are particularly sensitive in the neighbourhood of the boiling point of the filling material and, in consequence of their small capacity for heat, rapidly acquire the temperature of their surroundings. The thermal after effects observed with liquid thermometers are absent. Their readings are perfectly trustworthy as long as air has not leaked into them; this can be readily tested by cooling them in liquid air when the tension sinks to zero except in those cases in which methane is used. It should, however, be noted that the instrument records the temperature of the coldest part. H. W.

Vapour Pressure Regularities. VI. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 216—218. Compare this vol., ii, 302).—It has been shown by Rechenberg that, by applying Dühring's formula, it is possible to calculate from the vapour pressure curves of different substances the temperature at which the vapour pressure becomes zero (A., 1920, ii, 587). It might be expected that the temperature, in absolute degrees, corresponding with zero pressure, would be a constant fraction of the boiling temperature at atmospheric pressure. This fraction has been calculated for

the substances for which Rechenberg has given the zero vapour pressure point, and the values obtained approximate to a constant. Thus for substances with vapour pressure curves of the hexane type, some of the values found are: hexane, 0·40; benzene, 0·405; aniline, 0·450; phenol, 0·478; nitrobenzene, 0·436; ammonia, 0·466; carbon disulphide, 0·380; chlorine, 0·379; whilst for substances of the water type were found water, 0·496; glycerol, 0·534; ethyl alcohol, 0·515; butyric acid, 0·500. The constancy found, however, is not of the same order as that obtained for the ratio of the absolute boiling points at different temperatures for different substances, and the opinion is ventured that Dühring's vapour pressure rule is only a useful empirical guide, and that no theoretical importance attaches to the zero vapour pressure point as calculated from it. E. H. R.

Boiling Point Relationships. RICHARD LORENZ and W. HERZ (*Zeitsch. anorg. Chem.*, 1921, **115**, 100—104).—According to the Guldberg-Guye rule, the boiling point of a liquid in absolute degrees at atmospheric pressure is equal to two-thirds of the critical temperature in the same units. The ordinary pressure is, however, no definite fraction of the critical pressure, and calculations have now been made to see whether a definite relationship exists between the boiling points at definite fractions of the critical pressure and the critical temperature. The fractions of the critical pressure employed were $\frac{1}{33}$ and $\frac{1}{50}$, and it was found, in the case of a large number of organic liquids, that a better constant was obtained for T_s/T_c, where T_s is the boiling point and T_c the critical temperature, when T_s was taken at a definite fraction of the critical pressure, $\frac{1}{50}$ giving a better constant than $\frac{1}{33}$. Inorganic liquids, of which only three were dealt with—water, nitrogen, and hydrogen sulphide—all gave low values of the constant, compared with organic liquids. A good constant was also obtained when the boiling points were compared at $2\frac{1}{2}$ times the critical density. E. H. R.

The Relation between Boiling Point in the Vacuum of the Cathode Light and Critical Temperature. P. WALDEN (*Zeitsch. anorg. Chem.*, 1921, **115**, 312).—An acknowledgment that part of the author's conclusions published under this title (A., 1920, ii, 665) were anticipated by Hansen (A., 1910, ii, 827). E. H. R.

Comparative Study of Fractionating Still-heads. NEIL PRESTON MOORE (*J. Physical Chem.*, 1921, **25**, 273—303).—An historical discussion of the various forms of still-head in use, both with and without temperature control, is entered into. These instruments have been used in the fractionation of mixtures of chloroform 75% and carbon tetrachloride 25% and the efficiency has been determined. The influence of certain factors on the fractionation has been noted and from the results of the experiments the author has constructed a new form of still-head which is far more efficient than any other yet described. All analyses of carbon tetrachloride and chloroform mixture were made by a

refractometric method which is described in the paper. The new still-head is made entirely of brass; it consists of two strips of brass, a bed plate 36 in. long, 6 in. wide, and $\frac{1}{16}$ in. thick, and a cover plate of the same dimensions except that the thickness is $\frac{1}{32}$ in. These plates are rounded at the ends. The bed plate carries 120 slotted angle strips made of 26 gauge metal and $\frac{1}{4}$ in. apart. Each strip is 6 in. $\times \frac{3}{16}$ in. with $\frac{1}{8}$ in. "turn up." This "turn up" is provided with slots $\frac{3}{32}$ in. deep and $\frac{1}{32}$ in. wide, so that each strip constitutes a dam $\frac{1}{32}$ in. high completely across the bed plate. The slots serve as open sluices through which the overflow liquid can travel down the still-head. The number of slots increases from the top of the still-head to the bottom; the top seven strips having five slots, the second seven strips having ten slots, and the number of slots increasing by five for each successive seven strips until the bottom seven has each ninety slots. The bed plate and cover plate are joined together by a strip of $\frac{1}{8}$ in. square brass rod which runs continuously round the plates and thus completely closes it in. At the lower end a brass tube $\frac{5}{8}$ in. diam. is soldered and this receives the vapour from the distilling flask; at the upper end a tube 6 in. long and $\frac{1}{2}$ in. diameter serves as the delivery tube. The still-head is usually set at an angle of 45° to the vertical, but this may be varied. Working with this apparatus under normal conditions, it is found that the efficiency of fractionation is increased from 47·8%, the best obtainable with the cylindrical still-heads, to 82·7%. J. F. S.

Fractional Distillation with Contact Ring Still-heads. R. LESSING (*J. Soc. Chem. Ind.*, 1921, **40**, 115—119$_T$).—The still-head is prepared from glass tubes 2·5—4·0 cm. wide and 40—150 cm. long which are drawn out into as wide a constriction as practicable at the lower end; it is packed with cylindrical rings of approximately equal height and diameter ($\frac{1}{4}$ inch) having a gap in the circumference and a more or less diametrical partition connected on one side with the cylinder but out of touch on the opposite side. They are disposed indiscriminately in the column at the angles which they find when dropped promiscuously into the vessel. In order to obtain the best contact between the liquid and vapour phase and to keep all surfaces well irrigated, it is desirable to induce as much return-flow as is compatible with the drainage capacity of the column and the avoidance of excessive back-pressure; this is conveniently effected by lagging the still-head with asbestos, cotton-wool, or corrugated cardboard and providing a reflux condenser which allows the required portion of the vapour to pass uncondensed and to distil over whilst the bulk is condensed and returned, copiously wetting the still-head.

Comparative experiments with mixtures of benzene and toluene and with fusel oil show that the new still-head is considerably more efficient in separating power than any of the usual types. This is attributed to the large surface per unit of volume, which affords ample opportunity for condensation of the vapours and re-evaporation of the condensate and to the turbulence created by

the frequent deflection of the currents of vapour and condensate which can only flow in any one direction for a distance of a quarter of an inch or less. H. W.

Constitution and Heat of Combustion. OTTO H. BINDER (*Chem. Zeit.*, 1921, **45**, 477—478).—The author discusses the relation between the constitution of organic compounds and their heat of combustion, the latter affording useful information regarding the constitution. In the case of isomerides, where the bonds are so arranged that they have equal heat values, the results obtained by calorimetric measurements must be the same. W. P. S.

Heats of Combustion and Formation of Nitro-compounds. I. Benzene, Toluene, Phenol, and Methylaniline Series. W. E. GARNER and C. L. ABERNETHY (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 213—235).—The heats of combustion and formation of a large number of nitro-derivatives of benzene, toluene, phenol, and methylaniline have been determined. A number of heats of crystallisation and nitration of some of the substances have also been determined. The present results, together with the most trustworthy values of previous investigators, are examined with the object of calculating the heat change occasioned by the entry of a nitro-group in the series examined. It is shown that the heats of formation of the nitro-compounds are markedly influenced by the position of the nitro-groups, and there is no regular change in these values similar to that observed in the introduction of a CH_2-group into aliphatic compounds; no empirical equation can be devised showing the relationships between the heats of formation of all aromatic nitro-compounds. It is shown that certain regularities exist between the heats of formation and nitration of the four series examined. The heat of combustion in all the series decreases with increase in the number of nitro-groups, but the heat of formation tends to a maximum for the second or third member of the series, and then diminishes. An exception is seen in the benzene series, but here it is probable that the maximum is shifted to the fourth member of the series, and that the same general relationship would hold if the more highly nitrated benzenes could be obtained and examined. A regularity is observed in the heats of formation of the di- and tri-nitro-derivatives of toluene, and this is expressed by the formula $H=30{\cdot}8-1{\cdot}3(n\times 4m\epsilon)$, where n is the number of nitro-groups ortho to the methyl group and m the number of nitro-groups ortho to a nitro-group. The introduction of the methyl group into benzene to form toluene modifies only slightly the shape of the curves showing the heat of formation of the nitro-compounds, but the introduction of an hydroxyl- or methylamino-group has a marked effect. The curves for the phenol- and methylamino-group are very much alike, which indicates that energy changes involved in the nitration are similar in the two cases. The heat of nitration curves for these substances are straight lines. There is no simple additive relationship for the entry of nitro-groups into benzene and toluene. The differences between the benzene and toluene derivatives on the one hand and the phenol and methylaniline derivatives on the

other are connected with the relative ease of nitration. In the three first-named series the nearer the nitro-groups are to one another the greater is the strain in the molecule and the lower the heat of formation. The sensitiveness of nitro-compounds to impact and their comparative instability run in line with their heats of formation; thus 2 : 3 : 4-trinitrotoluene which has the lowest heat of formation is the most sensitive to impact. The stability of the unsymmetrical trinitrotoluenes and benzenes is less than that of the symmetrical forms.

The large heat of formation of the nitrophenols is a disadvantage from the point of view of their employment as explosives, although this is to some extent balanced by their comparatively high oxygen content. Thus although trinitrotoluene contains 29% less of the oxygen necessary for complete combustion than does picric acid, yet its heat of detonation is similar, 924 cal./gram compared with 914 cal./gram (water gaseous in both cases). This is to be expected from the lower heat of formation of trinitrotoluene (128 cal./gram) compared with that of picric acid (277 cal./gram). In this example, the introduction of the hydroxyl group into benzene to form phenol is accompanied by the absorption of more energy than that of the methyl group to form toluene, and this is reflected in the explosion phenomena. The present figures show that the fifth member of a series has a very low heat of formation. The effectiveness of tetryl as an explosive is very largely dependent on its being the fifth member of the methylaniline series, and thus possessing a low heat of formation. The entry of the fourth nitro-group into the side chain does not affect this uniformity. Of the isomeric trinitrotoluenes, 2 : 3 : 4-trinitroluene is shown to have the lowest heat of formation, that is, it contains the lowest internal energy, whilst 2 : 4 : 6-trinitrotoluene has the highest heat of formation. If on detonation these two substances gave the same products of decomposition, the former would have an advantage over the latter of 54 cal./gram. For the same reason, *as*-trinitrobenzene would be a more powerful explosive than the symmetrical compound.

J. F. S.

Temperature and Degree of Polymerisation. W. Herz (*Zeitsch. anorg. Chem.*, 1921, **115**, 237—240).—It is shown that the assumption that the ratio of molecular volume to density at corresponding temperatures for non-associated and associated liquids is constant leads to incorrect results. For monohalogenated benzenes, the ratio d_s/d_c, where d_s is the density at the boiling point and d_c that at the critical temperature, is 2·69. On the above assumption, $M_c/M_s = 2{\cdot}69 d_c/d_s$ for any liquid, where M_c and M_s are the molecular weights of the liquid at the corresponding temperatures. The ratio M_c/M_s for a number of known associated liquids, calculated from the above equation, is found to be very nearly unity. The same result was obtained taking other corresponding temperatures (equal fractions of the critical temperature) for comparison. It is concluded that the theory of corresponding states cannot be applied in cases where change of molecular state may occur. E. H. R.

An Empirical Law of the Molecular Volumes of the Halogens and their Compounds for all States of Aggregation. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1921 **115**, 241—252).—It was shown by Fajans and Grimm (this vol., ii, 168) that when the molecular volumes of the haloids of one alkali metal are plotted against those of the corresponding haloids of another alkali metal, a straight line is obtained. It has now been found that straight lines are obtained when, against the molecular volumes of potassium chloride, bromide, and iodide as abscissæ are plotted as ordinates the molecular volumes of a great variety of halogen compounds. Not only simple and complex metallic chlorides, bromides, and iodides, but also a large number of crystalline chloro-, bromo-, and iodo-benzene derivatives were found to follow the same rule with remarkable precision. Fluorine derivatives do not generally fall into line with the other halogen compounds, and divergences are found when the molecular weights of the compounds of the halogens exceed about 200. The rule applies also to the liquid halogens and their hydrogen acids when the molecular volumes at their boiling points are compared. Similar relationships could not be found between the molecular volumes of compounds of other "homologous" or isomorphous series, for example, the sulphates, selenates, and chromates. In the course of the work, fresh determinations were made of the densities of magnesium chloride (d_4^{25} 2·32), magnesium bromide (*d* 3·72), magnesium iodide (*d* 4·255), aluminium chloride (*d* 2·41), *p*-chloroaniline (*d* 1·36—1·38), *p*-bromoaniline (*d* 1·763), and *p*-iodoaniline (*d* 2·07—2·11). E. H. R.

Analysis of Molecular Volumes from the Point of View of the Lewis-Langmuir Theory of Molecular Structure. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1921, **43**, 991—1004).—A theoretical paper in which an analysis of molecular volumes, as determined from the critical data, has been made from the point of view of the Lewis-Langmuir theory of molecular structure and particularly of Langmuir's theory of isosteres. Evidence is brought forward to show that isosteric molecules and nuclear atoms in hydrogen compounds have the same volume. The volume depends, therefore, on the number and arrangement of electrons surrounding the positive nucleus of the atoms rather than on the charges on the nucleus, that is, on the particular kinds of atoms concerned. Thus, it has been shown that the nuclear carbon, nitrogen, and oxygen atoms of methane, ammonia, and water respectively have the same volume. The carbon atoms in ethane, ethylene, and acetylene have volumes increasing with the degree of unsaturation. The same observation holds in comparing the carbon atoms in benzene and *cyclo*hexane. The volumes of atoms thus increase with the number of electron pairs shared. An explanation of this is presented. It is shown that elementary nitrogen and carbon monoxide probably have the normal or acetylenic structure, three pairs being shared, rather than the condensed structure suggested by Langmuir. A structure is suggested for nitric oxide and the volumes of the inactive gases are considered from the point of view of Langmuir. J. F. S.

Some Factors Governing the Sorptive Capacity of Charcoal. Sorption of Ammonia by Coco-nut Charcoal. JAMES BRIERLEY FIRTH (Trans., 1921, **119**, 926—931).

Stoicheiometry of Adsorption. I. Adsorption of Kations of the Alkalis and Alkaline Earths. SVEN ODÉN and HUGO ANDERSSON (*J. Physical Chem.*, 1921, **25**, 311—331).—The adsorption of alkali nitrates by charcoal has been determined, and it is shown that the amount of kation and anion adsorbed is equivalent in all cases; the statements to the contrary which are found in the literature are to be explained by the presence of acid or alkali left in the adsorbent after purification. From the isothermals the order of adsorption is $Li<Na<K<Rb<NH_4<Cs$. Hence it follows that in this series the amount of adsorption increases with the atomic weight of the kation. In the case of the nitrates of the alkaline earths, the order of adsorption is $Mg<Ca<Sr<Ba$, which follows the same rule as the alkali nitrates. The measurements were all made with a Zeiss interferometer which determines the change in concentration after adsorption. The method of using the instrument for this purpose is fully described in the paper. The authors attempt to express the adsorbed quantity as a function of the remaining concentration by means of the Freundlich formula $y=kc^{\beta}$; using concentrations between 0·1 and 0·8 mol. per litre; it is found that k decreases from $4{\cdot}4\times10^{-3}$ for cæsium to $1{\cdot}31\times10^{-3}$ for sodium, whilst β increases slightly with decreasing atomic weight of the kation; the same type of relationship is also found with the nitrates of the alkaline earths. J. F. S.

The Reversibility of the Reaction $CaCO_3=CO_2+CaO$. PIERRE JOLIBOIS and BOUVIER (*Compt. rend.*, 1921, **172**, 1182—1183).—Using the method previously described (*ibid.*, 809) for registering the dissociation pressure of a compound, the authors have studied the conditions for reversing the dissociation of calcium carbonate. Calcium carbonate in various forms was used, and after heating to effect the dissociation, it was found that in no case on cooling was the reversal of the reaction complete. When, however, a mixture of precipitated calcium carbonate with excess of calcium oxide was used, complete reversal could be attained on cooling. W. G.

Crystallising Power of Compounds of High Molecular Weight. R. O. HERZOG and K. BECKER (*Zeitsch. physiol. Chem.*, 1921, **112**, 231—235).—General considerations without experiments. G. B.

Anisotropic Liquids. J. STEPH. VAN DER LINGEN (*J. Franklin Inst.*, 1921, **191**, 651—677).—With the object of ascertaining whether the pseudoisotropic layers of Lehmann and Bose have a space lattice, as is contended by Vorländer, molten layers of *p*-azoxyanisole, *p*-azoxyphenetole, anisaldazine, and active amyl cyanobenzylideneaminocinnamate have been allowed to solidify in

a magnetic field of 5000 gauss and the solidified layers examined as to their *X*-ray figures by Laue's method. The results show clearly and definitely that the pseudoisotropic layers of Lehmann and Bose do not possess homogeneity of structure as this term is understood in crystallography, nor is there any evidence to show that such layers are microcrystalline. Consequently, it is concluded that the experiments show that such layers do not possess a space lattice; that is, Vorländer's contention, based on the optical phenomena of such layers, cannot be accepted. The uniform dispersion, which was observed in all cases, is due to the regularity of molecular structure of these anisotropic liquids, probably caused by similarly oriented ellipsoids only one of the axes of which is fixed in space.

J. F. S.

A Theory of Slow Hydrolysis of Salts. A. Tian (*Compt. rend.*, 1921, **172**, 1179—1181).—On the basis of the presence of colloidal suspension in cases of slow hydrolysis of salts, the following theory is proposed. The colloidal material, at first in extremely fine particles, will give, spontaneously by union of these particles, larger and larger granules which, for a given weight, will have a smaller and smaller surface. The hydrolysis of the salt will be limited by two reactions, produced by the salt and the water at the expense of the acid and base liberated. The first, occurring only in the aqueous phase, will be a reaction taking place solely between the ions, and will be the reverse of hydrolysis. The second, which may be considered as a supplementary retrogression, will occur between the insoluble phase and the aqueous liquid by action of the other soluble element of the salt. It will also be a saturation of the acid by the base, but effected between two phases. The velocity of this action will be smaller as the surface of separation becomes more limited. It will diminish therefore as the colloidal solution evolves, and, the hydrolysis being less and less limited, the decomposition of the salt will progress. The hydrolysis will be slow because the evolution of the colloidal solution will itself be slow.

W. G.

A Cause of Dispersion of the Colloid in an Important Class of Hydrosols. A. Tian (*Compt. rend.*, 1921, **172**, 1291—1293).—Solutions of salts, the base of which is only slightly soluble, constitute hydrosols consequent on hydrolysis. In such hydrosols there is a special cause of stability which permits, within wide limits, of the reversibility of their transformations. This special cause is due to the spontaneous dispersion of the colloidal metallic hydroxide, which itself results from a chemical action. In the immediate neighbourhood of the colloid the retrogression of the hydrolysis is much more marked than in the rest of the aqueous phase. The excess of salt thus reconstituted diffuses away from the generating layer and then undergoes normal hydrolysis, giving again the metallic hydroxide temporarily dissolved and thus the dispersion of the colloid progresses. This theory is applied to certain phenomena.

W. G.

The Stability and the Reversibility of the Transformations of the Hydrosols obtained by Hydrolysis of Salts. A. TIAN (*Compt. rend.*, 1921, **172**, 1402—1404. Compare preceding abstract).—It has been shown (*loc. cit.*) that, in the hydrosols resulting from the slow hydrolysis of salts of heavy metals in solution, the hydroxide in colloidal suspension is continually divided and dispersed by a chemical process, and it is to this cause that the marked stability and the reversibility of the transformation of these hydrosols are due. These colloidal solutions are stable in the presence of electrolytes which normally flocculate pure hydrosols. The colloidal particles are capable both of uniting and dividing as already shown, and hence these hydrosols exhibit reversible colloidal transformations. W. G.

A Colloid Theory of the Corrosion and Passivity of Iron, and of the Oxidation of Ferrous Salts. JOHN ALBERT NEWTON FRIEND (Trans., 1921, **119**, 932—949).

Chemical Reactions and Radii of Curvature. R. LUCE (*Compt. rend.*, 1921, **172**, 1287—1288. Compare Reboul and Luce, *ibid.*, 197).—Further experiments are quoted in support of the view that the chemical action of a liquid on a solid depends on the shape of the latter, being greatest at those points where the mean curvature is greatest. Thus the influence of curvature is the same in liquids and in gases. W. G.

Chemical Affinity. A. KOREVAAR (*J. Physical Chem.*, 1921, **25**, 304—310).—A theoretical paper in which the author points out that the term affinity is used in the literature and in text-books in two senses, thereby causing considerable confusion. On the one hand, it is used to designate the force acting between combining atoms, this is, the classical definition, and on the other, it is used to express the thermodynamic conception, created by van't Hoff, which defines it as the maximum external work done by the chemical reaction at constant temperature and volume. The author reviews the use made of the term in a number of standard text-books and recommends that the term affinity should be used only in its classical sense, whilst the maximum external work should always be referred to as such and never as affinity. J. F. S.

Determinations of the Number of Independent Constituents of a System of Substances. F. WALD (*Bull. Soc. chim.*, 1921, [iv], **29**, 266—271. Compare Dubreuil, A., 1920, ii, 742).—The mathematical expression worked out by Dubreuil is developed so as to deal with more complex systems. H. J. E.

The Phenomenon of Partition. NICOLAS DE KOLOSSOVSKY (*Bull. Soc. chim. Belg.*, 1914, **28**, 257—264).—A study of the partition of hydrogen peroxide between water and ethyl ether. As the total concentration, P, increases, the coefficient of partition, C, between these two solvents at 18° diminishes, its value being given by $C=14{\cdot}77-0{\cdot}397P+0{\cdot}00432P^2$. If m and n represent the degrees

of association of hydrogen peroxide in the water and ether respectively under these conditions, then it is calculated that the ratio $n/m=1{\cdot}3$, a value which is very close to that previously found for acetic acid in the same solvents (A., 1911, ii, 591). W. G.

Equilibrium in the System: Ammonia–Ammonium Nitrate–Ammonium Thiocyanate. H. W. FOOTE and S. R. BRINKLEY (*J. Amer. Chem. Soc.*, 1921, **43**, 1018—1031).—The vapour pressures have been determined at 0°, 10°, and 20° for the two binary systems ammonia–ammonium nitrate and ammonia–ammonium thiocyanate and also for three mixtures in the ternary system ammonia–ammonium nitrate–ammonium thiocyanate. The range of vapour pressure investigated was that from the saturated solutions to those showing pressures of about 1600 mm. Neither double salts nor solid products with ammonia are formed at 0° or above; but the saturated solutions are in equilibrium with the simple salts. The solubility curves of ammonium nitrate and ammonium thiocyanate in the three-component system have been determined at 0°, 10°, and 20°, together with the univariant point at which these curves intersect. The results show that, at the temperatures investigated, curves of equal vapour pressure in the ternary system are very nearly straight lines which connect points of equal vapour pressure in the two binary systems. The vapour pressures of the solutions examined are far below those required by Raoult's law. At any temperature, the saturated solution, containing ammonium nitrate and ammonium thiocyanate in approximately the molecular ratio 1 : 3, shows the lowest vapour pressure, and this solution must therefore be most efficient for absorbing ammonia from gaseous mixtures. J. F. S.

Equilibrium in the System: Ammonia–Water–Ammonium Thiocyanate. H. W. FOOTE (*J. Amer. Chem. Soc.*, 1921, **43**, 1031—1038. Compare preceding abstract).—The vapour pressure of solutions of ammonia in water have been determined at 0°, 10°, and 20°, and those of water, ammonia, and ammonium thiocyanate have been determined at 10°, 20°, and 30°. The solubility of ammonium thiocyanate in water and aqueous solutions of ammonia (3·49%—22·70%) has been determined at 10°, 20°, and 30°. No additive or double compounds are formed between ammonium thiocyanate and either water or ammonia. The results show that at the temperatures investigated curves of equal vapour pressure in the ternary system are very nearly straight lines which connect points of equal vapour pressure in the two binary systems. J. F. S.

The System: Copper–Cupric Oxide–Oxygen. H. S. ROBERTS and F. HASTINGS SMYTH (*J. Amer. Chem. Soc.*, 1921, **43**, 1061—1079).—A continuation of work previously published (this vol., ii, 98). The present paper deals with the measurement of the dissociation pressures of the liquid mixture of the two oxides of copper throughout the range where this solution is in equilibrium with cuprous oxide; the composition of the liquid in equilibrium

with solid cupric oxide from the eutectic temperature to 1230° and with solid cuprous oxide from the eutectic temperature to the minimum melting point of cuprous oxide; the measurement, at 1120° and 1150°, of the dissociation pressures for different compositions of the liquid when no solid phase is present; and measurements of the dissociation pressures of cuprous oxide within the temperature range where a liquid rich in copper is a dissociation product. It is shown that solid solution between cupric oxide, cuprous oxide, and copper is either non-existent or negligible. In conjunction with the determinations of Heyn (A., 1904, ii, 406) and Slade and Farrow (A., 1912, ii, 1057), the *TX* (melting point) relations from pure copper up to the mixture 81% cupric oxide 19% copper have been established. The general course of the *PT* curves in the system has been deduced from a consideration of the *TX* diagram. Data are presented for the three dissociation-pressure curves in the system Cu_2O–CuO–O_2; the melting point of the Cu_2O–CuO eutectic is shown to be 1080·2° at 402·3 mm.; and the melting point of cuprous oxide is 1235° at 0·6 mm. The energy changes for the reaction $CuO(s) \rightleftharpoons \frac{1}{2}Cu_2O(s)+\frac{1}{4}O_2(g)$ and the heat of fusion of cuprous oxide have been calculated from the data.

J. F. S.

Application of the Law of Mass Action to the Results obtained in the Action of β-Galactosidase on Galactose in Solution in Propyl Alcohol. MARC BRIDEL (*Compt. rend.*, 1921, **172**, 1288—1291).—When the law of mass action is applied to the synthesis of propyl β-galactoside by the action of β-galactosidase on galactose in solution in aqueous propyl alcohol containing from 35—70% of the alcohol, it is seen that equilibrium is not reached even after several months.

W. G.

Velocity of Chemical Reactions. JOHN EGGERT (*Zeitsch. angew. Chem.*, 1921, **34**, 181—183).—A lecture dealing with the study of chemical kinetics from the experiments of Guldberg and Waage up to the present day.

J. F. S.

The Oxidation of Arsenious Acid by Nitric Acid in Presence of Mercuric Ions; the Change of a Negative Catalyst to a Positive. ALFONS KLEMENC and FRIEDRICH POLLAK (*Zeitsch. anorg. Chem.*, 1921, **115**, 131—140).—The influence of mercuric nitrate at different concentrations on the velocity of oxidation of arsenious acid by nitric acid has been studied, by titrating the unchanged arsenious acid with iodine solution at regular intervals during the progress of the reaction. Preliminary experiments showed that the effect of mercury ions was to tend to inhibit the reaction. For the quantitative experiments the greatest care was needed to avoid contamination with impurities to obtain concordant results. At a concentration of $7·7\times10^{-6}$ mols. per litre the effect of the mercuric ions was to inhibit the reaction completely. With diminishing concentration the inhibiting effect became less marked down to a concentration of $7·7\times10^{-8}$, and at $7·7\times10^{-9}$ mols. per litre there was a positive catalytic effect, which

became still more marked at $7 \cdot 7 \times 10^{-11}$ mols. per litre. The positive catalytic effect at extreme dilutions is shown by the fact that when a blank experiment was repeated in a vessel which had been previously used for an experiment in presence of mercuric ions, the flask having been cleaned with great care, the reaction was still accelerated by traces of mercuric salt remaining. The sensitiveness of the reaction to the catalyst is extraordinary, as previously the smallest recorded effective concentration for catalysis was 7×10^{-6} mols. per litre of colloidal platinum in the decomposition of hydrogen peroxide. The effect of mercury in reducing the activity of palladium hydrosol recorded by Paal (A., 1918, ii, 303) is probably due to the negative catalytic action of the mercury. Mercury either as metal or in the ionic condition probably exerts a negative catalytic effect in oxidation processes generally.

E. H. R.

Influence of Physical Conditions on the Velocity of Decomposition of certain Crystalline Solids. C. N. HINSHELWOOD and E. J. BOWEN (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 203—212. Compare A., 1920, ii, 743).—The conditions governing the rate of decomposition of crystalline substances have been examined. It is shown that the rate of decomposition of silver permanganate at 110° depends on the size of the particles. In the case of crystals of average size 0·25 mm. × 0·027 mm., the velocity is greatly accelerated as the reaction proceeds, owing to the disintegration of the crystals, whilst with finely powdered material consisting of particles of 0·005 mm. diameter the initial velocity is much greater but the subsequent acceleration is much less. The conditions ruling the propagation of the decomposition from the surface of a crystal to the interior have been studied in the case of the decomposition of ammonium dichromate and potassium permanganate by heat. It is shown that if the decomposition products do not form a coherent film round the crystal the reaction proceeds without hindrance and may be strongly accelerated owing to the disintegration of the crystals, but if a film is formed the reaction is greatly retarded. With increasing temperature, the retardation becomes less and less marked and is succeeded by the usual type of accelerated reaction. This retardation is observed in the case of ammonium dichromate, but not in the case of potassium permanganate, because here the products are not firmly held. In the case of solid solutions of potassium permanganate in potassium chlorate, the retardation is observed in the initial stages of the decomposition. The connexion between the velocity of decomposition of particles of different sizes is not the same as that between the linear magnitudes, but considerably less. This implies that the surface which is effective in determining the rate of reaction is considerably greater than the apparent surface as deduced from the linear size of the particles. What appear to be individual crystals are really aggregates which are sufficiently loosely held together to allow decomposition to take place between them. The rate of evolution of oxygen from isomorphous mixtures of potassium permanganate and potassium

chlorate, of a series of compositions, has been determined at temperatures of 148—230·2°, and values have been deduced for 200° in each case. The temperatures employed are not high enough to decompose the chlorate, so that the permanganate is responsible for the evolution of the oxygen. From the results, the authors calculate the heat of activation for the equimolecular mixture and find the value 618 cal./gram-mol. potassium permanganate at 200°, or 309 cal./gram-mol. of the equimolecular mixture. The results show that no distinction can be drawn between physical and chemical forces. The chemical forces between the atoms of solid substances are profoundly modified by physical conditions, such as proximity to the surface, and by the presence of neighbouring atoms in the space lattice. Moreover, the decrease in potential energy attending the process of solid mixture leads to increased chemical stability in a way which can be calculated approximately from the heat of mixture. J. F. S.

Hydrolysis of Dichloro- and Hexa-aquo-chromic Chlorides. ARTHUR B. LAMB and GORTON R. FONDA (*J. Amer. Chem. Soc.*, 1921, **43**, 1154—1178).—The uncertainty of the present values of the hydrolysis constants of the dichloro- and hexa-aquo-chromic chlorides has been pointed out. The hydrolysis constant of the dichloro-chloride has been measured by two methods. The first is a modification of the Walker method, and involves a comparison of the conductivities of solutions of the dichloro-salt containing different amounts of hydrochloric acid. The second is a method already applied by Bjerrum to this problem, and involves a study of the kinetics of the transformation of the dichloro-compound into the hexa-aquo-compound, and in particular of the variation of the velocity constant of this reaction with the concentration of the hydrogen ion in solutions to which acid has been added. Knowing this variation, it is possible to compute the hydrolysis constant from the observed values of the velocity constant in pure aqueous solution. The value obtained by the first method is $K_g=1{\cdot}8\times10^{-6}$, by the second $K_g=2{\cdot}0\times10^{-6}$, which give the mean value $K_g=1{\cdot}9\times10^{-6}$. It has been pointed out that the addition of small amounts of dichloro-chromic chloride to a solution and the observation of its change in conductivity offers a convenient method for the determination of hydrogen-ion concentrations, particularly when they are small, and that the results are not affected by the presence of chloride ions at a concentration equal to that of the dichloro-chloride (0·008*M*). The hydrolysis constant of the hexa-aquo-chloride at 25° has been measured over a wide range of concentrations by five methods. An average value of $K_b=1{\cdot}58\times10^{-4}$ at 25° was obtained, with an average deviation of less than 5%. Incidentally, in applying the method depending on the rate of inversion of sucrose, it was necessary to determine the acceleration produced by 0·0074*M* acid at 25°, a much lower concentration than had previously been worked with at this temperature. In applying the Walker method to the hexa-aquo-chloride, it was also necessary to determine the location of the equilibrium between the dichloro-

chloride and the hexa-aquo-chloride at a concentration of 0·008*M*, both in the presence and absence of hydrochloric acid. It was found that in the former case 1·5% and in the latter 0·25% of the dichloro-salt was present in the equilibrium mixture at 25°.

J. F. S.

The Catalytic Action of certain Metallic Salts in Reactions of Organic Compounds. ANTOINE KORCZYŃSKI (*Bull. Soc. chim.*, 1921, [iv], **29**, 283—290; Willgerodt, A., 1887, 806; Slator, Trans., 1903, **83**, 729; Gay, Ducelliez, and Raynaud, A., 1914, i, 946).—An attempt is made to find a relation between catalytic action and atomic weight. Preparations of *p*-nitrophenyl thiocyanate and brominations of benzene have been carried out with various metallic salts as catalysts, and the yield obtained is compared with the atomic weight of the metal the salt of which is used. It is claimed that a certain periodicity is observed. H. J. E.

Action of Hydrolytic Diastases. MARC H. VAN LAER (*Bull. Soc. chim. Belg.*, 1920, **29**, 214—227).—Diastatic catalysis is a form of catalysis by hydrogen ions and the reaction velocity depends solely on the ratio enzyme/substrate. Within certain limits, the velocity increases with concentration of hydrogen ions. W. P. S.

Dimensions of the Atom. L. ST. C. BROUGHALL (*Phil. Mag.*, 1921, [vi], **41**, 872—876).—When the atomic diameter is calculated from b of van der Waals's equation by the relation $\sigma=(3b/2\pi N)^{\frac{1}{3}}$, where $N=2{\cdot}75\times10^{19}$, it is found that the increase in passing from one inert gas to the succeeding one is constant: helium 2·30, argon 2·86, krypton 3·14, xenon 3·42 ($\times10^{-8}$ cm.). This regularity is not found when the diameters are calculated from the viscosities. The regularity found is in agreement with Langmuir's theory.

J. R. P.

The Arrangement of the Periodic System of the Elements. GEORG SCHALTENBRAND (*Zeitsch. anorg. Chem.*, 1921, **115**, 127—130).—An attempt to explain the derivation of the periods of elements by an " extension " of the first hydrogen–helium period. In the derived period, in place of a hypothetical homologue of an element of the first period, a number of new elements appear which share the properties of the hypothetical element. E. H. R.

Natural Systems for the Classification of Isotopes, and the Atomic Weights of Pure Atomic Species as related to Nuclear Stability. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1921, **43**, 1038—1060. Compare A., 1920, ii, 479, 745).—In an earlier paper (*loc. cit.*) the different atomic species were classified in series according to the composition of the nuclei of their atoms. The series are (1) thorium, (2) uranium, (3) lithium, and (4) metachlorine ($Cl\ 17^{37}_{3}$). The present paper adds two natural and experimentally determined methods of classification, which are complementary, (1) according to the isotopic number, and (2) according to the class number as defined further on. It is found that five variables, P, the atomic weight, or total number of protons

in the nucleus; N, equal to $P-M$, the number of negative nuclear electrons; M, the atomic number, or the net positive charge on the nucleus; N/P, which may be considered as the relative negativeness to positiveness of the nucleus; and n, the isotopic number, determine the composition of the atomic nuclei. These five variables would give ten two-dimensional curves, but the representation is greatly simplified by the fact that by a proper choice of the two independent variables (n and M) constant values of all five may be represented as straight lines. The isotopic number represents the number of neutrons of the formula pe necessary to represent the excess in the composition of the nucleus over what may be considered as the normal composition represented by the isotopic number, 0, which may be given as $(p_2e)_M$. The isotopic number is exactly twice the value of the function f in the Harkins-Wilson equation for atomic weights or $W=2(M+f)=2M+n$. The atomic species were classified according to their f values in an earlier paper (*loc. cit.*). The isotopic number 0 seems to represent the lowest isotope which is stable both with respect to disintegration and to aggregation, and includes about 70—80% of all known material. However, all isotopes with the isotopic number are not supposed to be stable. The isotopic numbers higher than 0 are represented by 54 hyperbolas when N/P and P are the independent variables, and by 54 straight horizontal lines when n is plotted on the Y axis. It is shown that the composition of any atom is $(p_2e)_M(pe)_n e_M$. The relative abundance of the atomic species of the different isotopic numbers on the earth and in meteorites is, $n=0$, earth 84·5%, meteorites 79·0%; $n=1$, earth 13·0%, meteorites 5·3%; $n=2$, earth 0·2%, meteorites 1·6%; $n=3$, earth 0·007%, meteorites 0·0; $n=4$, earth 2·2%, meteorites 12·4%; $n=5$, earth 0·046%, meteorites 0·1%. Thus the abundance is very high for the isotopic number 0, decreases to a minimum in isotopic number 3, rises to a secondary maximum in 4, and again decreases to 5 and 6. The difference of 4 isotopic numbers between the maxima corresponds with 4 neutrons or a helio-group, which is an α-particle plus two electrons, so that it indicates that in this range, as well as in the radioactive region, the α-particle is an important unit in atom building. In an α-disintegration the isotopic number remains constant; in β-disintegrations, it is lowered by two. β-Disintegrations of atoms of odd atomic number are in general much more violent than those of even atomic number. Nuclei may be classified into the four following classes which bear an important relation to nuclear stability: (1) both N and P even, comprising about 90% of known material, (2) N even and P odd, 5%; (3) both N and P odd, 2·5%, and (4) N odd, P even, 0·0%, where all percentages are atomic. Therefore $P-N$, or the atomic number is even for most atoms, and the atomic weights of elements of odd atomic number are almost always odd, whilst those of even atomic number are usually even. The number of isotopes of elements of even atomic number should be, according to the earlier theory of the author, considerably larger than the number of isotopes of elements of odd atomic number. On the basis of the relations in this and what has been said above,

the existence of a number of undiscovered isotopes is predicted. The general theory indicates that the number of isotopes per atomic number reaches a maximum somewhere in the region between atomic numbers 28 and 83, and that there are fewer isotopes in the radioactive region, and very many less in the region of few isotopes between atomic numbers 1 and 27. A system of nomenclature of the radioactive atomic species is put forward. The atomic weights of isotopes of odd atomic number are almost always odd numbers, in order to make the number of negative nuclear electrons an even number. However, the values of the N/P ratio for lithium of atomic weight 7 and boron of atomic weight 11 are so high that the presence of lower rather than higher isotopes is indicated by the theory; thus indicating that lithium has an isotope of atomic weight 6, and that boron has an isotope of atomic weight 10. Whilst these isotopes have been discovered, the author's prediction of their existence was made in an earlier paper before their discovery. The existence of isotopes of these elements with still lower atomic weights than these would be contrary to the general rule that N/P is never less than $\frac{1}{2}$ for stable complex atoms. The isotopes of even atomic number should have atomic weights which are mostly even numbers, although some odd atomic weights may occur. Thus most isotopes differ in atomic weight by 2. It is suggested that groups, such as the p_2e group, which contain one negative electron may be extremely stable with respect to disintegration, but that they tend to combine with each other and with other similar groups, or even with negative electrons alone, to form more complex groups in which the number of negative electrons is even. Thus two p_2e groups would combine to form an α-particle, or one p_2e group would unite with a negative electron to form a p_2e_2 group or double neutron. Thus such groups including Rutherford's p_3e, if it exists, would be stable with respect to disintegration, but not with respect to aggregation. In exceptional cases a p_2e group might attach itself to a larger atom nucleus, thus forming the isotope of lithium of atomic weight 6 by combining with one α-particle; that of nitrogen by combining with 3 α-particles and that of boron by a union with 2 α-particles. There are many facts which suggest that the disintegration of an atom need not be the exact reversal of its method of formation. J. F. S.

A Rotary Burner. GEORG LOCKEMANN (*Zeitsch. angew. Chem.*, 1921, **34**, 198).—A rotary burner for mechanically keeping in continual motion a Bunsen flame for use in such laboratory operations as ashing organic substances, distilling liquids, etc., consists of a horizontally rotating wheel driven by a motor or water turbine, on which is mounted vertically the burner tube in such a manner that the distance radially from the axis of rotation can be adjusted at will. The vertical tube is connected with a horizontal gas lead through an enlarged T-piece, forming a gas-tight socket in which it is capable of rotating. To avoid possible gas leaks at this joint, the gas is allowed to mix with air in the horizontal lead in the usual Bunsen burner fashion, so that should the socket become worn at

all, the suction of the flame will cause an inward flow of air instead of a gas leakage outwards. The whole apparatus is mounted on an ordinary iron laboratory stand, and several may be coupled in series by driving cords if desired, and all worked from the same motor. G. F. M.

Lecture Experiment: Reduction of Oleic Acid to Stearic Acid. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1921, **114**, 1—3).—One gram of oleic acid in 10 grams of glacial acetic acid is quantitatively reduced in five minutes, by shaking with 0·1 gram of platinum black in an atmosphere of hydrogen. C. R. H.

Inorganic Chemistry.

Determination of the Atomic Weight of Tellurium. P. Bruylants and G. Desmet (*Bull. Soc. chim. Belg.*, 1914, **28**, 264—266).—The starting material was pure tellurium prepared from hydrogen telluride. The tellurium was dissolved in nitric acid and the solution evaporated to dryness, the residue being calcined and melted. The tellurium dioxide was dissolved in pure aqueous sodium hydroxide and the tellurium estimated volumetrically either in alkaline or just acid solution by the method of Marckwald and Foïzik (A., 1910, ii, 604). The mean of twelve estimations in alkaline solution gave the value 127·8 for the atomic weight, and of nine estimations in acid solution the value 127·65.

W. G.

Method of Producing Dry Ammonia. H. W. Foote and S. R. Brinkley (*J. Amer. Chem. Soc.*, 1921, **43**, 1178—1179).—A convenient method of storing and delivering dry ammonia is described. The apparatus consists of a 500 c.c. wide-necked bottle fitted with a stopper carrying two tubes with taps, one for delivery and the other for charging. The bottle is nearly filled with dry ammonium thiocyanate, which acts as adsorbent. The bottle is surrounded by ice and the charging tube connected to an ammonia generator, the ammonia as it enters the bottle is absorbed about as rapidly as by water, and when the ammonium thiocyanate is saturated, it contains about 45% of its weight of ammonia. The ammonia can be drawn off by slightly raising the temperature, room temperature is generally sufficiently high. This method has the advantages that the rate of evolution of the gas can be readily controlled by slight changes of temperature and also the gas evolved is absolutely dry.

J. F. S.

Compounds of Ammonia and Carbonic Acid in Equilibrium with their Aqueous Solutions. Ernst Terres and Hans Weiser (*Zeitsch. Elektrochem.*, 1921, **27**, 177—193).—The conditions under which the different compounds of ammonia and

carbonic acid are stable in contact with aqueous solutions of the components have been studied at temperatures from 0·1° to 60°. Only ammonium hydrogen carbonate forms a congruent solution in water, that is, one in which the ratio of CO_2 to NH_3 is the same both in solution and in the solid phase. Of the other compounds of ammonia and carbonic acid, precise conditions were known only for the formation of ammonium carbamate, but in the course of the work methods were found for obtaining both the salt, $2NH_4{\cdot}HCO_3,(NH_4)_2CO_3,H_2O$, and normal ammonium carbonate in a pure state. The former salt crystallises from solutions containing ammonia and carbon dioxide in the ratio 4 : 5. Normal ammonium carbonate was prepared by dissolving 395 grams of ammonium hydrogen carbonate in 150 grams of water and 333 grams of 25% ammonia solution, whilst passing in ammonia under an increased pressure of 0·2 atm. and warming at 40° until solution was complete. On cooling to 10°, the normal carbonate crystallised.

For the equilibrium experiments, solutions were prepared starting with each of the above four substances as solid phases, by dissolving them in different concentrations of ammonia. Owing to the slowness with which equilibrium was attained in those cases where a change of solid phase occurred, it was necessary to prepare the solutions at a higher temperature in order to obtain complete solution and then allow the solid phase to separate on cooling to the required temperature. The concentrations of ammonia and of carbonic acid were determined in the solution when equilibrium was reached, and the solid phase was examined both by analysis and microscopically. It was found possible readily to identify by their crystalline form the five solid phases which were found to occur, namely, ammonium hydrogen carbonate, normal carbonate, hydrogen carbonate–carbonate double salt, carbamate and hydrogen carbonate–carbamate double salt, $NH_4{\cdot}CO_2{\cdot}NH_2,NH_4{\cdot}HCO_3$.

Equilibrium diagrams for each temperature were constructed by plotting carbon dioxide % against ammonia % in the solution; changes of direction of the curve indicated a change of solid phase. By combining the diagrams for different temperatures, a three-dimensional diagram was constructed in which the fields corresponding with the different solid phases were indicated. The normal carbonate and the two double salts have a limited temperature range of stability. Starting from ammonium hydrogen carbonate, between 0° and 33°, with increasing ammonia concentration, the solid phases change consecutively to the hydrogen carbonate–carbonate double salt, normal carbonate, and finally carbamate. At about 33°, both the double salt and normal carbonate disappear, but the new double salt hydrogen carbonate–carbamate appears between the hydrogen carbonate and carbamate. No further change appears up to 60°, the temperature limit of the experiments.

E. H. R.

Flocculation of Colloidal Arsenic Sulphide. Principle of a Method of Study. A. BOUTARIC and M. VUILLAUME (*Compt. rend.*, 1921, **172**, 1293—1296).—The spectrophotometric method

previously used to study the formation of precipitates (*Ann. Physique*, 1918, [ix], **9**, 183) has been applied to a study of the flocculation of colloidal arsenic sulphide. In order to have perfectly comparable flocculations, it is essential that the colloidal solution should not contain any free hydrogen sulphide or any free arsenious oxide. An excess of arsenious oxide has much less effect than an excess of hydrogen sulphide. The effect of free hydrogen sulphide varies with the nature of the electrolyte used as a flocculating agent. W. G.

Carbon Formed by the Action of Mercury on Carbon Tetrachloride, Tetrabromide, and Tetraiodide. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1921, **115**, 145—158).—By the action of mercury vapour on carbon tetrachloride at 600—700°, mercurous chloride is formed and carbon is deposited. Under high pressure, 900 to 2760 kilos per sq. cm., the reaction starts at about 400° and is accompanied by a fall in pressure. Carbon tetrabromide and tetraiodide react similarly. The carbon so formed retains water tenaciously, 7—10% after heating at 600° in a stream of nitrogen. The density of the carbon so obtained is high, 2·32 from carbon tetrachloride, 2·51 from the tetrabromide, and 2·37 from the tetraiodide, whilst that of graphite is 2·1—2·3. Carbon obtained similarly from hexachloroethane had d=2·16, from hexachlorobenzene 2·46 to 2·22, and from carbon disulphide 2·38. It appears that carbon formed by reactions not involving the formation of water has a higher density than that which is formed with water. On keeping, this dense form of carbon absorbs much water, and, when it is again dried, its density is found to have diminished. When carbon from carbon tetrachloride is heated for a short time at 2100—2300°, its density falls from 2·32 to 1·37. Chemically, the new, dense form of carbon is more reactive than sugar carbon (compare this vol., ii. 451). X-Ray examination failed to reveal crystalline structure, whilst sugar carbon appears to be to some extent crystalline. The high density of the new form of carbon is probably due to very close packing of extremely small particles. Heating to a high temperature causes the particles to increase in size with the result that the density decreases, without the appearance necessarily of a crystalline structure.

The condition diagram of carbon is discussed. The melting-point curve of graphite probably falls with increasing pressure, cutting the diamond curve near 1500°. The density of liquid carbon would then be greater than that of graphite. It is suggested that above the diamond field at high temperatures and pressures an unknown form of carbon exists, the density of which lies between that of graphite and diamond. Such a condition diagram accounts for the known properties of diamond and graphite and for the geological facts. E. H. R.

Oxidation of Carbon Monoxide by Passage with Oxygen or Air through the Silent Discharge and over Catalysts which decompose Ozone. ARTHUR B. RAY and F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1921, **43**, 967—978).—With the object of

finding a method for destroying carbon monoxide in air, the effect of passing this gas mixed with air or oxygen through an ozoniser and also over substances which catalyse the decomposition of ozone was studied. It is shown that the yield of ozone in the effluent gas by passing air or oxygen through a silent discharge is decreased by the presence of water vapour, by using a silvered electrode, and by having small arcs in series. There is an optimum rate of passage of the gas through the discharge, which in the present experiments is 7·72 litres per minute. This rate also gives the optimum formation of nitric acid. No appreciable oxidation of low concentrations of carbon monoxide in air or oxygen is effected by a low concentration of ozone unless the ozone is decomposed by special catalysts. Carbon monoxide may be almost completely oxidised by passage with pure oxygen or air through the silent discharge. The optimum conditions for obtaining maximum yields of ozone in the effluent gas are not necessarily the conditions for obtaining maximum oxidation. Other conditions being constant, the slower the rate of passage through the ozoniser the greater the amount of oxidation. The fact that under certain conditions more carbon monoxide is destroyed than can be oxidised by the maximum yield of ozone in the effluent gas when oxygen or air is ozonised under similar conditions, is accounted for by assuming the formation and decomposition of sufficient ozone in the ozoniser tube, or by assuming the formation of an active modification of carbon monoxide, or of oxygen other than ozone. The experimental evidence is insufficient to decide this point. By passing a mixture of air or oxygen containing relatively small amounts of carbon monoxide and ozone over a catalyst, such as silver, the carbon monoxide is readily oxidised, presumably as a result of the catalytic decomposition of ozone. Lead and lead dioxide are less effective catalysts, and manganese dioxide, unless specially prepared, is ineffective as a catalyst for the oxidation reaction, although it completely decomposes ozone. The carbon monoxide is most efficiently oxidised as regards time and energy when it is passed with air or oxygen through the silent discharge and over the silver catalyst. The best results are obtained when the undried air mixture is passed through a very large discharge unit and over silvered asbestos. The total oxidation obtained is apparently greater than can be accounted for by the assumption that it is all caused as a result of simple ozone decomposition—one molecule of ozone oxidising one molecule of carbon monoxide. The formation of an active modification of carbon monoxide or of oxygen other than ozone under these conditions is possibly indicated. The presence of hydrogen does not affect the oxidation of carbon monoxide in these circumstances. J. F. S.

The Behaviour of Carbon towards Silicon. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1921, **115**, 141—144).—The reaction between silicon and different forms of carbon when a loose mixture of equal weights of the two is heated has been studied. The temperature at which the reaction starts varies with different forms of carbon.

With carbon prepared by the action of mercury on carbon tetrachloride at 450°, the reaction started at 1220°, with soot from turpentine at 1340°, with sugar charcoal at 1410°, and with graphite at 1390°. The reaction product from the carbon from carbon tetrachloride, after freeing from uncombined carbon, appeared from analysis to contain the compound SiC. It consisted principally of microscopic particles with a small quantity of very thin needles. The density of the particles varied between 2·4 and 2·8. After ignition, the density of the heavier particles increased to 3·0, whilst the density of carborundum is 3·12. By using a higher proportion of carbon in the mixture, and also by heating carbon with silica at 1600° in a carbon tube, similar products were obtained containing, however, a higher proportion of carbon than SiC, but less than SiC_2. Further investigation is needed to determine the nature of the crystalline phases present in these products.

E. H. R.

The Binary Systems of Lithium Orthosilicate with Zirconium Orthosilicate and Calcium Orthosilicate. ROBERT SCHWARZ [with A. HAACKE] (*Zeitsch. anorg. Chem.*, 1921, **115**, 87—99).—The melting point of pure lithium orthosilicate, 1249°, is lowered by the addition of zirconium orthosilicate in proportion to the concentration of the latter, up to 30 mol.% $ZrSiO_4$, at which composition a pure eutectic is formed, m. p. 1021°. As the proportion of zirconium orthosilicate is still further increased, the melting point again rises to a maximum at 1152°, the melting point of the compound $3ZrSiO_4,2Li_4SiO_4$. Further increasing the proportion of zirconium orthosilicate, the melting point falls as far as 70 mol.% $ZrSiO_4$, to rise again subsequently, but experiments could not be continued beyond this point, as the mixtures could not be fused in the furnace used. The two silicates do not form mixed crystals. The mixtures containing 50 mol.% or more of lithium orthosilicate are readily attacked by cold water, the others by boiling water. Those containing a high proportion of zirconium orthosilicate resemble extremely hard porcelain. The densities of the mixtures were determined. The density increases from 2·28 (Li_4SiO_4) to a maximum 4·024 for the binary compound, falls slightly, and again rises to 4·51 ($ZrSiO_4$). The molecular weight of zirconium silicate, calculated by the Raoult–van't Hoff formula from the depression of the freezing point of lithium silicate, corresponds with the simple molecule $ZrSiO_4$.

The system: lithium orthosilicate–calcium orthosilicate is more complicated than the above. From 0—20 mol.% Ca_2SiO_4, pure mixed crystals separate; from the latter point up to 30 mol.% Ca_2SiO_4, mixed crystals separate until the composition reaches 30% Ca_2SiO_4, corresponding with a pure eutectic, m. p. 1092°. Throughout the remainder of the series mixed crystals are formed with melting point maxima at 40 and 60 mol.% and minima at 50 and 70 mol.% Ca_2SiO_4. A polymorphous change is indicated by an arrest point which has its greatest duration at 932° with 50 mol. % Ca_2SiO_4. Density determinations and microscopic

evidence confirm the existence of a compound Li_4SiO_4,Ca_2SiO_4 stable only below this temperature. Other thermal changes occur within 20° of this temperature in mixtures containing 35—45 and 55—65 mol.% Ca_2SiO_4 respectively, but their nature remains unexplained. The density of the compounds Li_4SiO_4,Ca_2SiO_4 is 2·847. Thin sections of this composition show fairly large doubly refracting granules, optically positive, probably biaxial, showing extinctions parallel to the cleavage. E. H. R.

Metallic Hydrides and the Action of Hydrogen on the Metals. I. E. TOMKINSON (*Chem. News*, 1921, **122**, 241—243).—A summary of the literature dealing with calcium, barium, and strontium hydrides. J. R. P.

Formation of Compounds and Solubility in Systems of the Type: Sulphuric Acid–Metal Sulphate. JAMES KENDALL and ARTHUR W. DAVIDSON (*J. Amer. Chem. Soc.*, 1921, **43**, 979—990. Compare this vol., ii, 45).—A continuation of work previously described. The solubility of the anhydrous sulphates of calcium, barium, magnesium, zinc, iron (ous), iron (ic), mercury (ous), mercury (ic), silver, aluminium, nickel, lead, and copper in anhydrous sulphuric acid has been determined at temperatures from the eutectic point upwards. Freezing-point determinations have been made over a similar temperature range. The following compounds have been isolated: $BaSO_4,3H_2SO_4$; $CaSO_4,3H_2SO_4$; which exists in two crystalline modifications, $MgSO_4,3H_2SO_4$; Hg_2SO_4,H_2SO_4; $Ag_2SO_4,2H_2SO_4$ and Ag_2SO_4,H_2SO_4, which exists in two crystalline modifications with a transition point at 66°. Ferrous sulphate and zinc sulphate also form double compounds, but the exact composition has not been ascertained. In the other cases, no double compounds could be isolated. The molecular solubility in anhydrous sulphuric acid at 25° is found to be: $CaSO_4$, 5·16; $MgSO_4$, 0·18; $Al_2(SO_4)_3$, $<0·01$; $ZnSO_4$, 0·17; $FeSO_4$, 0·17; $Fe_2(SO_4)_3$, $<0·01$; $CuSO_4$, 0·08; Hg_2SO_4, 0·78; Ag_2SO_4, 9·11; and $HgSO_4$, 0·02. Nickel sulphate and lead sulphate have a very small solubility at this temperature. The compounds obtained in the present investigation are considerably less complex and less stable than those given by the sulphates of the alkali metals (*loc. cit.*). If the metals are arranged in order of the electromotive series, compound formation is seen to be dependent on the position of the metal with respect to hydrogen. Only those metals much above hydrogen (for example, lithium and potassium) and those much below (for example, silver) show extensive acid salt formation. As the zero point is approached from either side, the stability of the complexes decreases until finally no compounds can be isolated. Solubility relationships throughout the series are found to follow a similar course. The alkali sulphates and silver sulphate are extremely soluble in sulphuric acid, the sulphates of the metals less pronouncedly positive or negative are much less soluble; the sulphates of metals with electrode potentials near to the zero point are practically insoluble. J. F. S.

Revision of the Atomic Weight of Lanthanum. Analysis of Lanthanum Chloride. GREGORY PAUL BAXTER, MUNRO TANI, and HAROLD CANNING CHAPIN (*J. Amer. Chem. Soc.*, 1921, **43**, 1080—1085).—Two samples of lanthanum material were subjected to a prolonged series of crystallisations as double ammonium lanthanum nitrates. The material thus finally obtained was shown to be entirely free from the other rare earths by spectroscopic examination. The material was converted into the chloride through the oxalate and oxide. The crystals of chloride first obtained were recrystallised four times and dried by keeping in a vacuum desiccator over fused potassium hydroxide. When it could be dried no further by this method, it was heated at 85°, whereby most of the water of crystallisation was expelled; the temperature was then raised to 130° to expel the last molecule of water. When this was complete, the temperature was raised to 360° for some time and the preparation then rapidly melted at 1000°. The heating was all carried out in hydrogen chloride, and after the fused salt had solidified this was replaced by nitrogen and eventually by air. The pure material was then transferred directly to a weighing bottle. The analysis was carried out both volumetrically and gravimetrically by the method previously described for the determination of the atomic weight of praseodymium (A., 1915, ii, 263). From six determinations the ratio $LaCl_3 : 3Ag$ was found to be 0·757895, the extreme values being 0·757930 and 0·757841, from which the atomic weight is calculated to 138·914. Seven determinations of the ratio $LaCl_3 : 3AgCl$ lead to the value 0·570410, the extreme values being 0·570331 and 0·570543, which give the atomic weight as 138·912. This is lower than the accepted value, but since the presence of the usual companions of lanthanum, cerium, praseodymium, and neodynium would raise the apparent atomic weight, this value must be regarded as a maximum. In the calculations, the specific gravity of anhydrous lanthanum chloride is taken as 3·947. J. F. S.

The Influence of Cerium on the Properties of Aluminium and of some of the more important Light Metal Alloys. J. SCHULTE (*Metall u. Erz*, 1921, **18**, 236—240).—Addition of small quantities of cerium (under 1%) to aluminium and alloys of aluminium containing 3% Cu or 3·3% Mg increased the ductility without altering the other properties, but it was without effect on alloys containing 10% Cu or 4% Ni, or 25% Zn. The nitrogen content of pure aluminium was considerably reduced by addition of 0·2% Ce, but, contrary to previous statements, cerium does not remove silicon from aluminium. [Compare *J. Soc. Chem. Ind.*, 1921, July.] A. R. P.

The Calculation of the Positions of Eutectic Points and Solubility Limits in Systems containing Iron. KARL DAEVES (*Zeitsch. anorg. Chem.*, 1921, **115**, 290—292).—Tammann has shown that in mixed crystal series there are certain limiting compositions beyond which the mixed crystals are or are not attacked by chemical

agents, and that these limits are found where the atomic proportion of one constituent is $\frac{1}{8}$ or a multiple of this fraction (A., 1919, ii, 398). In binary systems containing iron, for example, iron with carbon, titanium, phosphorus, arsenic, or boron, it is now found that similar atomic or molecular fractions are of importance. For instance, in the iron–carbon system, pearlite, with 0·89% C, contains $\frac{1}{8}$ mol. of Fe_3C; the solubility limit for carbon, 1·75%, corresponds with $\frac{2}{8}$ mol. Fe_3C; and the eutectic point, 4·29% C, corresponds with $\frac{5}{8}$ mol. Fe_3C. These relations may throw light on the molecular structure of alloys. E. H. R.

The Velocity of Diffusion of Carbon in Iron. IRIS RUNGE (*Zeitsch. anorg. Chem.*, 1921, **115**, 293—311).—Experiments were made to determine the velocity of diffusion of carbon into iron by measuring the change of resistance of iron wire in a current of gaseous hydrocarbon at high temperatures. Illuminating gas diluted with hydrogen had little or no action; toluene diluted with nitrogen reacted slowly, more quickly when diluted with hydrogen, whilst a rapid action was shown by mixtures of benzene with nitrogen, light petroleum (b. p. 90—100°) with hydrogen, and hexane with nitrogen or hydrogen. The resistance–time curves were similar in character to the theoretical curve, assuming the diffusion of carbon to follow the diffusion law. At 900°, the diffusion coefficient of carbon in iron is about 2×10^{-7} cm.^{2}/sec. With an active gas, at 930°, 0·6 mg. of carbon passes through 1 sq. cm. of surface in the first three minutes. The resistance change due to 1% of carbon is 5·7% at 920°, 7% at 830°, and 40% at 18° of the resistance at the corresponding temperature. The velocity of cementation falls off rapidly with temperature and is inappreciable at 700°. When cementation takes place above 900°, γ-mixed crystals are formed, and the product is found to consist of cementite and pearlite. At 800°, the β-iron takes up carbon to form an equilibrium mixture of γ-mixed crystals containing about 0·3% of carbon and β-iron. Whether diffusion takes place in the gaseous form or as carbon cannot be affirmed, but the marked influence of hydrogen on the rate of diffusion points to the former. E. H. R.

The Nature of Subsidiary Valencies. XXV. Stability of Complex Kations with Varying Magnitude of Anions. FRITZ EPHRAIM and FRANZ MÜLLER (*Ber.*, 1921, **54**, [*B*], 973—978).—It has already been shown that very large anions render small kations eminently capable of additive reactions (A., 1920, ii, 378), but evidence of the regular increase of the stability of the kationic complex with increasing size of the anion has only been deduced in the case of the halogens. Similar experiments are now described with the group, SO_4, SeO_4, CrO_4, MoO_4, WO_4, the method consisting in allying the ion with the nickelhexammine complex and measuring the temperature at which the ammonia tension of the product thus formed is equal to the atmospheric pressure. The stability of the complex is found to be independent of the atomic volume of S, Se, Cr, Mo, and W, but to increase proportionally with the molecular volume of the corresponding trioxide.

If a mixture of freshly-precipitated nickel hydroxide and ammonium molybdate is saturated with ammonia, the *compound*, $[Ni(NH_3)_5H_2O]MoO_4$, is obtained in sapphire-blue, hexagonal crystals; it is transformed by ammonia at 120° into *hexammine-nickel molybdate*, the ammonia tension of which is equal to the atmospheric pressure at 116°. Under similar conditions, ammonium tungstate and nickel hydroxide give dark blue, hexagonal crystals of the *compound*, $NiWO_4,6NH_3,8H_2O$, which is transformed by a current of ammonia at 125° into the *tetrammine*; the latter is converted by ammonia at the ordinary temperature in the presence of a trace of moisture into the *hexammine*, $[Ni(NH_3)_6],WO_4$, which has an ammonia tension equal to the atmospheric pressure at about 120°. Hydrated nickel hexammine chromate, $NiCrO_4,6NH_3,4H_2O$, pale green, quadratic crystals, is most readily obtained by solution of basic nickel chromate in concentrated ammonia and precipitation with alcohol; its constitution, however, appears to require further investigation. A mixture of this compound and the *substance*, $NiCrO_4,5NH_3,H_2O$, is obtained by the action of ammonia on a paste of nickel hydroxide and potassium chromate. *Nickelhexammine selenate* is prepared similarly from nickel hydroxide and sodium selenate, an intermediate aquo-ammine being obtained which is dehydrated in a current of ammonia at 100° and subsequently saturated with the gas at the ordinary temperature; its dissociation temperature is 168°. H. W.

Titanium Peroxide. MAURICE BILLY (*Compt. rend.*, 1921, **172**, 1411—1412).—From estimations of the active oxygen it is shown that all the compounds previously considered as salts of the oxide, TiO_3, are really complexes of hydrogen peroxide and pertitanic salts corresponding with the peroxide, Ti_2O_5. A complex double *potassium* salt was prepared having the composition $K_2SO_4,TiOSO_4$, and when it was dissolved in ice-cold water and alcohol added, the clear liquid decanted from the precipitate was found to contain hydrogen peroxide. A hydrate of the peroxide, $Ti_2O_5aq.$, was also obtained by precipitation with alcohol from a solution prepared by pouring equimolecular quantities of potassium sulphate and titanyl sulphate into an excess of hydrogen peroxide. W. G.

Atomic Weight of Germanium. JOHN H. MÜLLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1085—1095).—The processes of purification of the germanium salt used for the determination of the atomic weight of this element embodied a more thorough treatment for the elimination of the known impurities of germanium than previously adopted. The chlorine–hydrochloric acid distillation process, although adequate for the removal of silica and tin, can scarcely be accepted as a means of eliminating the last traces of arsenic from germanium compounds. Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last trace of arsenic. The treatment of the nearly pure germanium oxide with sufficient water to dissolve nearly all of it, and the fractional crystallisation of the hydrated

oxide from this solution, served a twofold purpose: to remove the much more soluble arsenic oxide at one end and to eliminate any remaining traces of tin and silica in the less soluble fractions at the other end. The formation of potassium germanofluoride was not carried out until the absence of the isomorphous stannofluoride and silicofluoride was ensured by complete removal of tin and silica from the original oxide. The stability of potassium germanofluoride and its non-hygroscopic character together with its complete decomposition in hydrogen chloride indicates that it is the most suitable germanium compound for accurate analysis. The complete conversion of the germanofluoride by hydrogen chloride, the germanium chloride volatilising, potassium chloride only being left, was established in all analyses by negative tests for both germanium and fluorine. The mean of seven determinations of the ratio $K_2GeF_6 : 2KCl$ gave 72·418 for the atomic weight of germanium, the extreme values being 72·41 and 72·45.

J. F. S.

Double Catalysis of Vanadic Acid and Hydrogen Peroxide. V. AUGER (*Compt. rend.*, 1921, **172**, 1355—1357).—Pervanadic acid resembles perchromic acid in that its catalytic decomposition of hydrogen peroxide, the pervanadic acid being itself reduced to a vanadyl salt, becomes more rapid and more complete in the presence of an acid. Vanadyl salts, however, unlike chromium salts, are immediately oxidised to pervanadic acid in the presence of hydrogen peroxide, so that in the course of time the whole of the hydrogen peroxide introduced into an acid solution of vanadic acid is completely destroyed and the reduction of the vanadic acid is more or less marked, according to the hydrogen-ion content of the solution.

W. G.

Alkali Pentachloro- and Pentabromo-ruthenates [Ruthenochlorides and Ruthenobromides]. A. GUTBIER, F. FALCO, and TH. VOGT (*Zeitsch. anorg. Chem.*, 1921, **115**, 225—236).—Experiments were made to determine the degree of hydration of these salts, about which observers have disagreed. The salts were prepared from $H_2[RuCl_5]$ and $H_2[RuBr_5]$ and the corresponding alkali chlorides and bromides. Potassium ruthenochloride always crystallises in the hydrated form K_2RuCl_5,H_2O. It does not form a hexachloro-salt with chlorine, unlike the organic halogen salts of ruthenium. When dehydrated by heat, it decomposes. The corresponding rubidium salt contains one molecular proportion of water, but the cæsium salt was always obtained in the anhydrous form except on one occasion, when the monohydrate was obtained. The salts are sparingly soluble in water, forming yellow solutions which darken gradually at ordinary temperatures, quickly at the boiling point. The hydrolytic change is accompanied by an increase in electrical conductivity (compare Howe, A., 1904, ii, 665). Of the ruthenobromides, the potassium and cæsium salts crystallise in the anhydrous form, the rubidium salt with one molecular proportion of water.

E. H. R.

Mineralogical Chemistry.

Tetrahedrite, Triplite, Anthophyllite, etc. EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1920, **58**, 437—453).—Crystallographic notes are given of anglesite, calcite, and datolite from various American localities. Crystals of tetrahedrite from the Hypotheek mine, Pine Creek district, Idaho, gave, after deducting 13·57% of quartz :

Sb.	As.	Fe.	Cu.	Zn.	Ag.	S.	Total.
26·81	trace	5·13	37·70	3·87	trace	26·49	100·00

Massive, brownish-red triplite, resembling garnet in appearance, occurring with dark-blue tourmaline in a lithia-rich pegmatite at Chatham, Connecticut, contains rather more iron and has higher refractive indices (α 1·665, β 1·673, γ 1·682) than triplite from Nevada (A., 1913, ii, 715); analysis gave :

P_2O_5.	MnO.	FeO.	CaO.	MgO.	F.	H_2O.	Insol.	Total (less O for F).
32·81	52·40	4·95	3·18	0·58	9·09	0·35	1·17	100·70

A brown, fibrous and bladed mineral from Chesterfield, Massachusetts, closely resembling cummingtonite in appearance, is proved to be the gedrite variety of anthophyllite (anal. I). Under the microscope it is colourless, except where stained with limonite; α 1·644, γ 1·660. The bucholzite variety of sillimanite (anal. II) is found as sheets of white to pale green, finely fibrous material in

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
I....	49·66	6·74	1·23	18·09	0·05	3·38	18·62	1·56	99·33
II....	38·10	59·48	1·05	—	—	—	—	1·32	99·95
III....	45·12	6·29	23·67	5·93	trace	trace	9·36	9·12	99·49

pegmatite at Russell, Massachusetts; D 3·172—3·180, H 5, α 1·629, γ 1·635. Stilpnomelane altering to chalcodite (A., 1920, ii, 499) forms veins in diabase at Lambertville, New Jersey, as a very light, porous aggregate of greenish-brown or golden-brown scales (anal. III). L. J. S.

Palmierite from Vesuvius. FERRUCCIO ZAMBONINI (*Compt. rend.*, 1921, **172**, 1419—1422).—The original analysis of palmierite (A., 1907, ii, 628) showed a deficiency of sulphur trioxide for a normal salt and the formula has been in doubt. New material formed on recent lava in the crater of Vesuvius has the form of hexagonal scales with $a:c=1:3·761$; it is optically uniaxial and negative with ω 1·712(Na). Crystalline material was prepared artificially by heating for one hour at 1000° and slowly cooling a mixture of potassium, lead, and sodium sulphates (5 : 7·5 : 9). This has D 4·50, is optically uniaxial and negative with ω=1·71, and on analysis showed SO_3 33·62, PbO 47·48, K_2O 17·53, Na_2O 1·31= 99·94, corresponding with the formula $(K,Na)_2Pb(SO_4)_2$. Although

palmierite is closely related crystallographically to aphthitalite and the two occur intimately associated, they do not appear to form mixed crystals. L. J. S.

Synthetic Silicate Minerals. J. Koenigsberger and W. J. Müller (*Jahrb. Min.*, 1921, *Beil.-Bd.* **44**, 402—459).—A repetition of results already published (A., 1918, ii, 402) with remarks as to their bearing on natural occurrences in the drusy cavities of igneous rocks. L. J. S.

Amesite, Corundophilite, and Chromium-bearing Chlorites. Earl V. Shannon (*Proc. U.S. Nat. Mus.*, 1920, **58**, 371—379).—Amesite (A., 1920, ii, 261) and corundophilite occur with diaspore, etc., in the emery mine at Chester, Massachusetts. The dark green corundophilite crystals gave anal. I, corresponding with $6(Mg,Fe)O,2(Al,Fe)_2O_3,3SiO_2,5H_2O$; refr. indices α 1·600, β 1·603, γ 1·610. A lavender-coloured chlorite with uvarovite on chromite from Newcastle, Eldorado Co., California, gave II, corresponding with $10RO,2R_2O_3,5SiO_2,6H_2O$; α and β 1·582, γ 1·593. A dark purplish-red chlorite with chromite from Deer Park, Wyoming, gave III; $6RO,R_2O_3,4SiO_2,4H_2O$; α 1·587, β and γ 1·590. These two chromium-bearing chlorites are almost optically uniaxial and are near to kämmererite.

	SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I....	23·20	24·42	—	3·48	13·40	1·04	22·76	12·00	100·30
II....	29·36	18·81	1·53	—	1·65	2·20	35·67	11·34	100·56
III....	32·12	9·50	7·88	—	1·98	1·24	35·36	10·25	100·37*

* Including chromite 2·04%.

L. J. S.

Minerals from the Tungsten Mine at Trumbull, Connecticut. Earl V. Shannon (*Proc. U.S. Nat. Mus.*, 1920, **58**, 469—482).—Analyses and optical data are given of the following: I, Prochlorite, friable aggregates of greenish-black vermiform crystals; formula $2FeO,2MgO,Al_2O_3,2SiO_2,2H_2O$. II, Epidote, ash-grey prisms resembling zoisite but with the crystal-angles of epidote. III, Muscovite, var. margarodite, occurring as pearly, radiating scales as an alteration product of topaz. IV, Margarite, snow-white, pearly, and fibrous, occurring with margarodite and topaz; formula $CaO,2Al_2O_3,2SiO_2,H_2O$. V, Scapolite, brownish-white, columnar aggregates with fluorite. These minerals, except the first, all contain fluorine, and the last in unusual amount; the presence of a fluor-meionite is assumed in isomorphous mixture.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	F.	H_2O.	Total.
I.	23·69	21·26	—	26·52	0·43	3·32	17·60	—	—	—	7·63	100·45
II.	36·89	28·50	5·92	0·52	0·02	27·26	0·21	—	—	0·60	1·29	101·21
III.	46·88	36·42	1·98	0·82	trace	1·77	1·36	6·24	0·38	n.d.	4·03	99·88
IV.	33·72	50·27	0·66	trace	trace	10·48	0·47	1·64	0·74	0·14	1·90	100·02
V.	51·38	25·22	trace	—	trace	15·16	0·73	1·20	2·86	2·74	0·55	101·82*

* Including Cl 1·98.

L. J. S.

Orientite, a New Hydrous Silicate of Manganese and Calcium, from Cuba. D. F. HEWETT and EARL V. SHANNON (*Amer. J. Sci.*, 1921, [v], **1**, 491—506).—This occurs as minute, brown crystals lining drusy cavities and as granular aggregates in manganese ores (psilomelane, manganite, etc.) at several places in the province Oriente, Cuba. The crystals are orthorhombic, with $a:b:c=0·6720:1:0·7916$. D 3·05, H 4½—5, α 1·758, β 1·776, γ 1·795. The mineral is readily soluble in hot hydrochloric acid with evolution of chlorine and separation of flocculent silica. Before the blowpipe it fuses to a black, blebby glass. The mean (anal. I; traces MgO,ZnO,Cl) of three analyses of material containing some black inclusions gives the ratios $4CaO,2Mn_2O_3,5SiO_2,4H_2O$, or as an orthosilicate $Ca_4Mn'''_4(SiO_4)_5,4H_2O$. Since, however, the water is expelled only near red heat the formula is written as $H_4Ca_4(MnOH)_4(SiO_4)_5$. The mineral shows some relations to the kentrolite group.

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	O.	CaO.	H_2O (<110°).	H_2O (>110°).	Total.
I....	32·48	1·08	1·56	29·92	3·27	22·47	0·03	7·93	98·74
II....	23·76	4·50		20·91	—	4·36	15·60	8·20	99·88

An associated brown, amorphous mineral, D 2·5, H 2½, optically isotropic with n 1·55, gave anal. II (also Mn_2O_3 21·31; insoluble 1·24). This seems to be a mixture of orientite and neotocite. L. J. S.

Analytical Chemistry.

Simple Method of Gas Analysis for Physiological Purposes. WILHELM TRENDELENBURG (*Zeitsch. Biol.*, 1920, **72**, 141—162).—Description of a single piece of students' apparatus, permitting the estimation of oxygen in blood, carbon dioxide in alveolar air, etc., with moderate accuracy. G. B.

A Hydrogen Electrode Vessel adapted for Titrations. A. BAIRD HASTINGS (*J. Biol. Chem.*, 1921, **46**, 463—466).—The electrode vessel, which is designed to render possible the measurement of hydrogen-ion concentration and the making of electrometric titrations without allowing the escape of volatile matter, is made in two portions, an upper, stationary part, to which a paddle-shaped electrode is attached, and a lower, rotating part. The two portions are connected by means of a mercury seal. The rotating vessel is closed at the bottom by a stop-cock with a right-angled bore, by means of which the solution under investigation enters the chamber and the stem connecting it with the exterior is filled with potassium chloride solution. Electrical connexion with the calomel electrode is effected by leaving a central band of the stop-

cock ungreased. The vessel is first filled with hydrogen and the solution under investigation then placed in it. A continual stream of the gas is unnecessary. Hydrogen-ion determinations of standard solutions made simultaneously with the Clark electrode and this apparatus agreed within one millivolt. E. S.

Method for the Estimation of the Acidity of Coloured Solutions. J. L. Lizius (*Analyst*, 1921, **46**, 194—195).—A filter-paper in a small Buchner funnel is moistened with phenolphthalein solution and the excess of the latter is removed by suction. The liquid under examination is titrated with standard alkali solution, the approximate end-point being ascertained by transferring drops of the solution to the filter-paper. The whole solution is then filtered; if the paper retains a pink coloration, too much alkali solution has been added, and it is treated with a small volume of standard acid and again filtered, these operations being repeated until the colour of the filter paper is changed by the addition of 0·05 c.c. of acid or alkali solution. W. P. S.

Detection and Estimation of traces of Hydrogen Peroxide. F. W. Horst (*Chem. Zeit.*, 1921, **45**, 572).—Hydrogen peroxide is estimated by reducing it with ferrous sulphate solution and determining the ferric sulphate colorimetrically by ammonium thiocyanate. As the ferrous solution must be absolutely free from ferric salts, it is placed in a closed Erlenmeyer flask and a current of hydrogen sulphide is passed first through the cold and then through the boiling solution, which is subsequently cooled in a current of carbon dioxide. Twenty c.c. of the sample to be tested are placed in a graduated tube, and a few c.c. of light petroleum added to form a layer above the sample and prevent oxidation during the reaction. After the introduction of 2 c.c. of the ferrous sulphate solution, the mixture is agitated by a current of carbon dioxide which must be previously freed from oxygen by passing it through ferrous sulphate solution. Five c.c. of a concentrated solution of ammonium thiocyanate solution are then added, and after further agitation the colour is compared with that of a known standard solution. W. J. W.

Estimation of Chlorine, Sulphur, and Phosphorus in Organic Substances. Ach. Grégoire and Em. Carpiaux (*Bull. Soc. chim. Belg.*, 1919, **28**, 331—335).—The method described is for use with plant products, and is a slight elaboration of that of Villiers (A., 1897, ii, 522). The material is digested with concentrated nitric acid and a little potassium permanganate in a specially designed apparatus, which is figured and described in the original. The sulphur and phosphorus remain in the flask as sulphuric and phosphoric acids, whilst the chlorine distils off along with nitrous fumes and is collected in water as hydrochloric acid. These three acids are then estimated by the usual methods. W. G.

Gasometric Estimation of Hypochlorites. Alexander Killen Macbeth (*Chem. News*, 1921, **122**, 268).—A gasometric method for estimating hypochlorites consists in treating them in a

van Slyke nitrometer with an alkaline solution of hydrazine, and measuring the nitrogen evolved. In absence of free chlorine trustworthy results are obtained. The available chlorine in bleaching powder may be estimated by this method. It has not proved suitable for estimating chlorates. W. J. W.

The Kjeldahl Method. H. W. Daudt (*J. Assoc. Off. Agric. Chem.*, 1921, **4**, 366—373).—Investigation of this method and its modifications showed that the proportion of sulphuric acid to alkali sulphate is important; with 10 grams of potassium sulphate or 8·2 grams of sodium sulphate, 20—25 c.c. of sulphuric acid effect the most complete decomposition of a substance. The time of boiling, apart from the preliminary digestion, should be at least two hours, unless a shorter period is known to be effective for any particular substance. A quantity of copper sulphate not exceeding 0·5 gram does not cause retention of ammonia, but copper sulphate is not as effective as mercury. Sodium thiosulphate may be used in place of potassium sulphide for decomposing ammonium mercury compounds. W. P. S.

Estimation of Ammoniacal Nitrogen in Fertilisers containing Calcium Cyanamide and Ammonium Salts. J. Froidevaux and H. Vandenberghe (*Ann. Chim. anal.*, 1921, **3**, 146—151).—A solution of the sample is treated with an excess of sodium hydroxide solution, and a current of air is drawn through the mixture and then passed through a known volume of standard acid; about seven hours are required to remove the ammonia from 0·25 gram of ammonium sulphate. The mixture is maintained at the ordinary temperature during the whole time and at the end of the operation the excess of the standard acid is titrated. W. P. S.

Colorimetric Estimation of Phosphoric Acid. Ach. Grégoire (*Bull. Soc. chim. Belg.*, 1920, **29**, 253—258).—Forty-five c.c. of a solution containing from 0·002 to 0·025 mg. of P_2O_5 and 2 c.c. of nitric acid (D 1·12) are treated with 2 c.c. of molybdic acid–quinine reagent, then diluted to 50 c.c., and the coloration obtained is compared with that of a standard mixture prepared under the same conditions. Small quantities of silica do not interfere, but iron should be removed previously by means of the "cupferron" reagent. The quinine reagent is prepared by dissolving 1 gram of quinine sulphate in dilute nitric acid, adding a quantity of barium hydroxide sufficient to precipitate the sulphuric acid, filtering the mixture, and adding the filtrate to a solution of 40 grams of ammonium molybdate in 500 c.c. of nitric acid (D 1·20); the whole mixture is then diluted to 1 litre. W. P. S.

A Gravimetric Method of Estimation of Small Amounts of Phosphoric Acid. Gustav Embden (*Zeitsch. physiol. Chem.*, 1921, **113**, 138—145).—A micro-method for the estimation of phosphate is described, depending on precipitation as strychnine phosphomolybdate (A., 1909, ii, 266). The method is applicable with accuracy to quantities of P_2O_5 from 1 mg. upwards; since the

precipitation is carried out in neutral or faintly acid solution, the method is suitable for the estimation of inorganic phosphoric acid in the presence of easily hydrolysable organic phosphoric acid compounds such as lactacidogen (compare also A., 1900, ii, 757; 1901, ii, 343; 1915, ii, 66). C. R. H.

Volumetric Estimation of Alkali Pyrophosphates. FRANZ LUTZ (*Magyar Chemiai Folyóirat*, 1919, **25**, 96—98; from *Chem. Zentr.*, 1921, ii, 949—950).—In the estimation of pyrophosphates soluble in water, a known excess of *N*/10-silver nitrate is added. After making up to a certain volume, the precipitate of silver pyrophosphate is removed by filtration and the silver remaining in the filtrate titrated with ammonium thiocyanate solution, using iron alum as indicator. It was found that the greater the dilution after the precipitation of the silver pyrophosphate the better were the results obtained, owing to the dissociation of double salts formed in more concentrated solutions. As silver pyrophosphate is soluble even in a 1% solution of sodium pyrophosphate, the solution of the latter is added in small quantities to the excess of silver nitrate solution with constant shaking. Any acidity must be carefully neutralised by addition of *N*/10-sodium hydroxide after precipitation, since silver pyrophosphate is soluble in the weakest acids. G. W. R.

Iodometric Estimation of Arsenic Acid. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 727—728).—The author disagrees with Fleury's contention that in the estimation of arsenates by treatment in acid solution with potassium iodide and titration of the iodine with thiosulphate, erroneous results are obtained, due to the action of dissolved oxygen on the iodide (A., 1920, ii, 448). W. J. W.

A Simple Method for the Direct Estimation of Sodium in Small Amounts of Serum. BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1921, **46**, 467—473).—In the estimation of sodium in blood as pyroantimonate (A., 1920, ii, 268), the sodium may be precipitated directly from the serum. E. S.

Sodium Salicylate as Reagent for the Microchemical Detection of Aluminium, Iron, Chromium, and Manganese. C. VAN ZIJP (*Pharm. Weekblad*, 1921, **58**, 694—698).—Sodium salicylate reacts with aluminium nitrate to form colourless needles which have a tendency to unite into spherical masses; excess of aluminium retards production of crystals, whilst in presence of excess of sodium salicylate the crystals dissolve. The reaction is improved by adding cæsium chloride, and is also rendered more definite by exposing the drop of the mixed solutions to the action of ammonia vapour, by which means formation of aluminium hydroxide is avoided. In solutions of aluminium salts, the presence of iron is indicated by the brown colour imparted to the crystals; there is no precipitation of hydroxide. On the other hand, whilst no hydroxide is at first formed with a mixture of aluminium and chromium salts, such precipitation occurs extensively as the drop

evaporates, together with production of colourless crystals. When both iron and chromium are present in the aluminium solution, brown crystals and a brown hydroxide precipitate are formed on evaporation. Manganese salts give no crystals with sodium salicylate, but when the mixed solutions are subjected to treatment with ammonia vapour, light-green needles are formed. With a suitable amount of sodium salicylate this reaction is very sensitive even in presence of zinc. W. J. W.

Comparison of the Analytical Methods used for Alloys: Estimation of Manganese in Cast-iron. F. GRAZIANI and L. LOSANA (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 148—152).—For the estimation of manganese in cast-iron, gravimetric methods are the most accurate, but are too long for ordinary purposes; the latter are best served by Campredon's modification (*Guide prat. chim. métall. l'essayeur*, 1909, 511) of the Volhard method [compare *J. Soc. Chem. Ind.*, 1921, July]. T. H. P.

Reaction of Tin Salts. G. BRESSANIN (*Ann. Chim. anal.*, 1921, **3**, 155).—A reaction published recently by Mazuir (A., 1920, ii, 197) had been described previously by the author (A., 1912, ii, 994; 1914, ii, 146). W. P. S.

Separation of Silicon, Tin, Titanium, and Zirconium by means of Sodium Carbonate. PAUL WENGER and JULES MOREL (*Ann. Chim. anal.*, 1921, **3**, 139—142).—A weighed mixture of the four oxides is fused with six times its weight of sodium carbonate for three hours; the mass is then boiled with water and the solution filtered. The filtrate contains the silica and a portion of the tin; it is evaporated with the addition of nitric acid, the resulting residue of silica and metastannic acid collected and weighed, and the silica separated subsequently by treatment with hydrofluoric acid. The insoluble portion, containing the titanium and zirconium oxides and the remainder of the tin, is ignited, weighed, fused with eighteen times its weight of potassium hydrogen sulphate, the fused mass boiled with water acidified with nitric acid, and the mixture filtered. Metastannic acid remains insoluble, whilst the zirconium and titanium oxides dissolve and are separated by treating the neutralised filtrates first with hydrogen peroxide to precipitate the zirconium and then with an excess of ammonia to precipitate the titanium. W. P. S.

The Iodometric Estimation of Mercaptans. J. W. KIMBALL, R. L. KRAMER, and E. EMMET REID (*J. Amer. Chem. Soc.*, 1921, **43**, 1199—1200).—A modification of the method of Klason and Carlson (A., 1906, ii, 255) gave excellent results with all the mercaptans analysed, both aliphatic and aromatic. Thirty-five c.c. of $N/10$-iodine solution in aqueous potassium iodide is measured into a 250 c.c. stoppered bottle. About 0·25 gram of the mercaptan in a stoppered weighing tube is added, and the bottle stoppered and well shaken to mix the two substances. The excess of iodine is titrated with $N/10$-thiosulphate solution, using starch as an indicator. W. G.

A Method of Applying to Plants the Biochemical Process for the Detection of Dextrose. M. BRIDEL and R. ARNOLD (*Compt. rend.*, 1921, **172**, 1434—1436. Compare A., 1920, ii, 337).—The leaves or other plant material are extracted with boiling alcohol, the extract being diluted with water and defecated with lead acetate. The excess of lead is precipitated by hydrogen sulphide and the filtrate from this is evaporated to dryness under reduced pressure at a temperature not exceeding 50°. The residue is extracted first with ethyl acetate and then successively with fresh portions of 95% alcohol. The alcoholic extracts are united and evaporated under reduced pressure in the presence of calcium carbonate. The residue is extracted with 50% methyl alcohol. In one portion of the extract the reducing sugars are estimated. To the rest emulsin is added and the mixture kept at 20°, the reducing sugars being estimated from time to time. A diminution in the amount of these present is indicative of the presence of dextrose in the plant material. W. G.

The Inversion and Estimation of Sucrose. A. R. ROSE (*J. Biol. Chem.*, 1921, **46**, 529—535).—A more detailed account of work previously described (A., 1918, ii, 247). E. S.

Estimation of Carbohydrates in Vegetable Foods. VICTOR C. MYERS and HILDA M. CROLL (*J. Biol. Chem.*, 1921, **46**, 537—551).—Soluble carbohydrates in the edible portions of vegetables and fruits are estimated by the Lewis-Benedict method as used by Rose (A., 1918, ii, 247). For the estimation of the total available carbohydrate a weighed quantity of the ground vegetable is first boiled with water, then ground to a paste and the starch hydrolysed by "taka-diastase." An aliquot part of the filtered solution is acidified with concentrated hydrochloric acid until about $0{\cdot}6N$ and the hydrolysis completed by boiling. After nearly neutralising with strong sodium hydroxide solution the estimation is completed by the method used for the soluble carbohydrates. A separate determination of the reducing sugar contained in the "taka-diastase" is made and a correction applied. The results of numerous estimations of carbohydrate in vegetables and fruits are given. E. S.

The Estimation of Bases Combined with Weak or Moderately Strong Acids and of very Weak Bases with Acids and Vice Versa. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1921, **115**, 168—180).—Although tropäolin-O and -OO are comparatively insensitive indicators to acids and alkalies, they are valuable for certain titrations for which more sensitive indicators are unsuitable, for example in the titration of an acetate of an alkali metal with an acid. In the titration of potassium acetate with hydrochloric acid, the change of hydrogen-ion concentration at the neutral point is rapid if normal solutions are used, but far more gradual with $0{\cdot}1N$- or $0{\cdot}01N$-solutions. Even with normal solutions, dimethyl-yellow gives an acid reaction when only 80% of the acetate is neutralised, but tropäolin-O gives a good end point, with an error of only 0·3%. Titrations should not be made with

solutions weaker than normal. A comparison solution consisting of a 0·5N-solution of acetic acid containing the same amount of indicator as the solution to be titrated is used to determine the end point. Salts of other weak acids having a dissociation constant smaller than 1—2×10^{-4} can be titrated similarly. Weak bases such as aniline, having a dissociation constant greater than 10^{-10}, can also be titrated with tropäolin-O as indicator. Very weak acids such as phenol, and salts of moderately strong bases, such as ammonium salts, can be titrated with sodium hydroxide, using the same indicator and a suitable standard for determining the end point. E. H. R.

Simultaneous Detection of Tartaric Acid, Oxalic Acid, and Formic Acid by Resorcinol and Sulphuric Acid. F. Krauss and H. Tampke (*Chem. Zeit.*, 1921, **45**, 521).—About 0·2 gram of resorcinol is dissolved in 5 c.c. of a dilute sulphuric acid solution of the mixed acids and 10 c.c. of concentrated sulphuric acid are then added so as to form a layer below the solution. The evolution of carbon monoxide and the formation of an orange-coloured ring at the junction of the two liquids indicate the presence of the formic acid; below this orange ring is a blue ring, due to the presence of the oxalic acid, and, when the lower part of the mixture is heated, a deep-red coloured ring below the blue ring denotes the presence of the tartaric acid. The solution to be tested must not contain carbonates, sulphides, iodides, bromides, or oxidising substances. W. P. S.

Determination of the Composition of Mixtures of Eugenol and *iso*Eugenol Benzoates by means of Melting Points. Phyllis Violet McKie (Trans., 1921, **119**, 777—779).

Bromometric Estimation of Salicylic Acid. I. M. Kolthoff (*Pharm. Weekblad*, 1921, **58**, 699—702).—The accuracy of the bromometric method for estimating salicylic acid has been investigated. For the estimation of small amounts of salicylic acid, such as weak solutions of approximately 0·008—0·012 mol. concentration, 25 c.c. are mixed with 25 c.c. of $N/10$-potassium bromate, 1 gram of sodium bromide, and not more than 5 c.c. of 4N-hydrochloric acid. After remaining for five to ten minutes in a stoppered flask, 5 c.c. of N-potassium iodide are rapidly added, and the mixture is titrated with $N/10$-thiosulphate; starch must be added only towards the end of the titration. The addition of alcohol, as in the bromometric estimation of phenol, may be omitted. W. J. W.

Applications of Complex-Chemistry to the Problems of Organic Chemistry. I. A New Method for the Titration of Enols in Keto-enolic Mixtures. Walter Hieber (*Ber.*, 1921, **54**, [*B*], 902—912).—The method depends on the formation of complex copper salts which are freely soluble in chloroform and quantitatively retained by this solvent in the presence of water and on the quantitative retention of copper acetate by water in the presence of chloroform which may also contain alcohol.

The stock copper acetate solution is prepared by dissolving the crystalline salt (50 grams) in water (1000 c.c.). A suitable quantity of this solution (generally 6—10 c.c.) is mixed with alcohol (about 12 c.c.) and chloroform (6—8 c.c.) and cooled to about $-10°$, thus giving a supersaturated solution, from which, however, nothing separates for some hours. A weighed quantity of the substance under investigation is dissolved in a little cooled alcohol, chloroform being added if necessary. The former solution is rapidly added to the latter, and the clear, transparent mixture is shaken and immediately poured into a separating funnel containing about 250 c.c. of water. The whole process can easily be effected in from five to ten seconds. The lower chloroform layer containing the enolic copper salt is run into a second separator and the funnel is washed with a little of the same solvent. The copper salt is decomposed with dilute sulphuric acid and the chloroform is removed; potassium iodide (2—3 grams) is added and the copper estimated by titration with $N/10$-thiosulphate in the presence of starch.

It is shown that enols react instantaneously with copper acetate solution, and that, under the conditions adopted, the keto-enolic equilibrium is not sensibly displaced by the liberated acetic acid or by the excess of copper acetate. Since, however, the enolic copper salts are very sensitive towards acid, it is essential to use an excess of copper acetate in order to hinder their decomposition by the liberated acetic acid. With pure enolic substances, it is sufficient if double the calculated amount of acetate is taken. With mixtures, however, such a relatively large excess has an enolising effect on the ketone, and, in these cases, the necessary quantity is best determined by preliminary experiments with varying amounts of acetate. Under these conditions, the effect of temperature and duration of experiment is much less marked than with the bromine titration method.

The results obtained with the copper acetate method are in good agreement with those of the bromine titration method in the cases of acetoacetic ester and analogous substances. In the instances of the oxalyl ketones, on the other hand, the former process yields considerably lower results than the latter.

In cases such as those of acetoacetic ester, diacetyl- (dibenzoyl-) succinic ester and formylphenylacetic ester, addition of bromine occurs equally with the *cis*- and *trans*-forms; an internally complex copper salt, however, can only result from the *cis*-form, so that it is expected that the new method may render possible the recognition and isolation of *cis*- in the presence of *trans*-forms, provided that an instantaneous transformation of the geometrical forms is not induced by the copper acetate. H. W.

Iodometric Estimation of Acetone. P. H. HERMANS (*Chem. Weekblad*, 1921, **18**, 348).—The chief factor affecting the accuracy of the iodoform method for estimating acetone in aqueous solution is the amount of potassium hydroxide added; with either excess or deficiency, the results are not quantitative. For volumes of 20 c.c. and 100 c.c. of aqueous acetone, the necessary amounts

of $1\cdot5N$-potassium hydroxide are 10—15 c.c. and 25—30 c.c. respectively; the conversion is then complete in one to two minutes in the first, and in three to five minutes in the second case. W. J. W.

The Turner Reaction for Gurjun Balsam. J. B. LUTHER (*J. Assoc. Off. Agric. Chem.*, 1921, **4**, 422—424).—The test described in the U.S. Pharmacopœia, and known as the Turner reaction for the detection of gurjun balsam in copaiba, is modified as follows in order to prevent the concentrated sulphuric acid charring the mixture and so obscuring the coloration. Four drops of the oil, 1 c.c. of glacial acetic acid, and 1 drop of 10% sodium nitrite solution are mixed and shaken with 2 c.c. of glacial acetic acid containing 5% by volume of concentrated sulphuric acid. If gurjun balsam is present, a violet coloration appears at once. Colorations which develop after the lapse of ten seconds are without significance. W. P. S.

Volumetric Estimation of Aniline by Diazotisation. TH. SABALITSCHKA and H. SCHRADER (*Zeitsch. angew. Chem.*, 1921, **34**, 45).—An aqueous solution containing about 1·5 grams of aniline in 100 c.c. is treated with an excess of sulphuric acid (at least 3 mols. of acid per mol. of aniline), cooled, and titrated with $N/1$-sodium nitrite solution. Potassium iodide–starch paper is used as an external indicator and the end point is denoted when a blue coloration persists for fifteen minutes after the last addition of nitrite. The reaction proceeds rapidly at first, but the velocity decreases considerably towards the end. About one hour is required for the titration. W. P. S.

Estimation of Urea. YNGVE FUNCKE (*Zeitsch. physiol. Chem.*, 1921, **114**, 72—78).—The solution of urea is treated with Millen's reagent; the gases evolved on warming the mixture are swept out of the reaction vessel by a current of carbon dioxide, passed through acid cupric chloride solution to absorb traces of nitric oxide, and led into a Schiff's nitrometer, where the volume of nitrogen is measured. C. R. H.

Direct Method for the Estimation of Dicyanodiamide. ERLING B. JOHNSON (*J. Soc. Chem. Ind.*, 1921, **40**, 125—126_T).—The method differs from the somewhat similar process advocated by Harger (this vol., ii, 224) in that it depends on the precipitation of the compound of dicyanodiamide (2 mols.) with silver picrate (1 mol.); urea and dicyanodiamidine do not interfere. When the sample under investigation contains 5—15% of dicyanodiamide nitrogen, 5 grams, or a correspondingly larger amount if less nitrogen is present, are placed in a 500 c.c. flask and 450 c.c. of water are added. If the sample is calcium cyanamide or other product containing lime, glacial acetic acid is added to bring all the lime into solution as acetate. By this means the nitrogenous compounds are dissolved much more rapidly and completely than without the acid, a small excess of which does not matter; stronger mineral acids isomerise the nitrogen compounds. The flask is shaken in a machine for three hours, the solution is made up to

500 c.c. and filtered; 5 c.c. of nitric acid (20%) are added to 100 c.c. of the filtrate followed by 20 c.c. of sodium picrate solution heated at 40° (7·5 grams of picric acid neutralised with sodium hydroxide and diluted to 100 c.c.). The solution is cooled to about 5° and titrated with *N*/22·4-silver nitrate solution, which is added drop by drop with constant shaking. About 2 c.c. more silver solution are used than is required by the amount of dicyanodiamide supposed to be present. The dicyanodiamide compound is precipitated in a more or less gelatinous form according to the amount of dicyanodiamide present. After being vigorously shaken, the mixture is allowed to remain with occasional agitation for fifteen minutes at 5°, after which it is diluted with cold water to 200 c.c., shaken, and filtered. The excess of silver solution used is estimated by titration with *N*/22·4-sodium thiocyanate in 100 c.c. of the filtrate after addition of a further 5 c.c. of nitric acid (20%) and about 2 c.c. of ferric sulphate solution (5%) as indicator. The influence of excess of silver nitrate and of varying amounts of nitric acid and calcium acetate has been investigated and it is found that, when working with calcium cyanamide, the use of 5 c.c. of nitric acid (20%) per gram of calcium acetate present and the addition of 2 c.c. excess of silver solution will give good results without any corrections, which, otherwise, depend largely on the personal equation. In the presence of chloride and soluble sulphides a blank test is necessary.

The formation of dicyanodiamide–silver complexes is not restricted to picric acid, but is typical of all nitrophenols which are soluble in water. *Compounds* of the silver salts of dinitrophenol, trinitroresorcinol, and trinitrocresol with one and two molecular proportions of dicyanodiamide have been isolated; of these, trinitroresorcinol appears to give a more nearly quantitative precipitation and better results than picric acid. H. W.

Reactions of Alkaloids with Silico- and Phospho-tungstic Acids. A. HEIDUSCHKA and L. WOLF (*Schweiz. Apoth.-Zeit.*, 1920, **58**, 213—218, 229—233; from *Chem. Zentr.*, 1921, ii, 840, 841).—The precipitates obtained with silicotungstic acid and dilute solutions of alkaloids are, with the exception of those from quinine and caffeine, of colloidal character; on addition of electrolytes, 1 to 3% hydrochloric acid, or alkali salts, or, in some cases, on keeping, flocculation takes place and they may be filtered. With silicotungstic acid in 0·01 *N*-solution in the presence of 1% of hydrochloric acid, sparteine, quinine, cinchonine, and nicotine give precipitates of the general formula,

$$SiO_2,12WO_3,2H_2O,2\text{Alkaloid}+\text{aq.},$$

whilst morphine, codeine, thebaine, and cocaine give precipitates of the general formula $SiO_2,12WO_3,2H_2O,4\text{Alkaloid}+\text{aq}$. In the cases of strychnine, brucine, narcotine, papaverine, colchicine, aconitine, and veratrine, the precipitates are more complex. With very small concentrations of electrolytes, the precipitates approximated to the second formula, but quantitative estimation was impossible owing to changes in composition on washing. Alkaloids the silico-

tungstates of which are only slightly altered by 0·1% sodium chloride solution can, in the absence of proteins, be estimated by treatment with a small excess of silicotungstic acid, standardised by sodium hydroxide and methyl-red, after addition of 1% sodium chloride. After filtering and washing, the excess of silicotungstic acid is titrated with sodium hydroxide and methyl-red.

Phosphotungstic acid behaves similarly with alkaloids. From 0·01*N*-solutions coniine and caffeine are precipitated in finely crystalline form. In the presence of less than 1% of hydrochloric acid, sparteine, quinine, cinchonine, and nicotine give precipitates of the general formula $2[P(W_2O_7)_6]H_7,3Alkaloid+aq$. The composition of the precipitates is influenced by the concentration of hydrochloric acid and by excess of phosphotungstic acid. The solubilities of alkaloid phosphotungstates and silicotungstates are affected in various ways by addition of hydrochloric acid and sodium chloride. Small amounts of alkaloids can be estimated nephelometrically, using the silicotungstates. G. W. R.

Colour Reaction for Aconite. S. MALLANNEH (*Analyst*, 1921, **46**, 193—194).—If a small crystal of potassium ferricyanide is placed close to a minute portion of aconitine or powdered aconite root and a drop of formic acid is added, a green coloration is obtained. The reaction is not given by morphine, atropine, digitaline, strychnine, eserine, or hyoscyamine. [Note.—The aconite mentioned appears to be the Indian variety, which contains ψ-aconitine but not aconitine.] W. P. S.

Estimation of Alkaloids in Cacao. ANTONIO CERIOTTI (*Anal. Soc. Quím. Argentina*, 1920, **8**, 400—403).—The material after removal of fat is treated with boiling 5% sulphuric acid. Colouring matters, tannins, and resins are removed by precipitation with 3% mercuric acetate and the filtrate after neutralisation with magnesia is evaporated to dryness with the addition of a little sand. The alkaloids (theobromine and caffeine) are then extracted, using a mixture of benzene and chloroform, and weighed. Caffeine can be separated by extracting the mixed alkaloids with carbon tetrachloride. [See also *J. Soc. Chem. Ind.*, 1921, 409A.] G. W. R.

Estimation of Caffeine in Yerba Mate, Coffee, Tea, Kola Nut, and Guaraná. TRIFÓN UGARTE (*Anal. Soc. Quím. Argentina*, 1920, **8**, 413—415).—Caffeine is estimated in yerba mate, coffee, tea, kola nut, and guaraná by the following method. On heating a weighed quantity of the substance in a 500 c.c. Kjeldahl flask, caffeine is disengaged in white vapours, which, however, are not allowed to escape. After cooling and repeated treatment with water and filtration, the combined filtrates are evaporated to dryness and the residue is dissolved in 2 c.c. of water. The aqueous solution is shaken with chloroform, the chloroform solution separated by filtration, and evaporated to dryness. The residue is then extracted with water, and after evaporation, the caffeine dried at 100 to 105°, and weighed. [See also *J. Soc. Chem. Ind.*, 1920, 408A.] G. W. R.

Chemico-toxicological Detection of Morphine. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1921, **60**, 2—5).—In the test given by Denigès for morphine (A., 1911, ii, 79), the copper sulphate and hydrogen peroxide may be replaced by potassium ferricyanide and ammonia, the reaction being then applicable to the detection of morphine in the blood and in non-putrefied organs of the body. It is found also that a dilute aqueous solution of blood is decolorised when treated under suitable conditions with ammonia and hydrogen peroxide, whereas in presence of morphine the original pink colour of the solution becomes more pronounced. Conditions are given for the application of the reaction of Denigès to the detection of morphine in the blood. The reaction is not given by either hydroxydimorphine, or the alkaloids accompanying morphine in opium, or by artificial derivatives of morphine, such as dionine and peronine. It is, however, distinctly given by heroine, notwithstanding Denigès's statement to the contrary; specific reactions are given for distinguishing heroine from morphine. [Compare *J. Soc. Chem. Ind.*, 1921, 446A.] T. H. P.

Estimation of Strychnine in Scale Preparations containing Quinine and other Cinchona Alkaloids. T. F. HARVEY and S. BACK (*Analyst*, 1921, **46**, 188—193).—The method recommended is a combination of Harrison and Gair's method (A., 1903, ii, 704; precipitation of quinine as tartrate with subsequent recovery of the strychnine) and Simmond's method (A., 1914, ii, 307). Ten grams of the sample are dissolved in 70 c.c. of water, 5 c.c. of *N*/1-sulphuric acid are added, the solution is nearly neutralised with ammonia, 30 grams of potassium sodium tartrate are added, and the mixture is again nearly neutralised with ammonia. The whole is heated at 100° for fifteen minutes, cooled, diluted to 100 c.c., and filtered after two hours. Fifty c.c. of the filtrate are rendered ammoniacal, extracted with chloroform, the chloroform solution is extracted with 10% (weight/volume) sulphuric acid, using 50 c.c. in all, and the acid solution is transferred to a separating funnel containing a plug of cotton-wool. Five c.c. of 4% potassium ferrocyanide solution are added and the funnel is filled with 10% sulphuric acid (to exclude air). After two hours, the liquid is drawn off through the cotton-wool filter, the strychnine ferrocyanide washed with 5% sulphuric acid, and then shaken with chloroform and ammonia. The chloroform extract is evaporated, the residue washed three times with 1 c.c. of ether, dried, and weighed. A correction of −1·7% is made to allow for the volume of the quinine tartrate precipitate. Quinidine and cinchonidine do not interfere; quinicine, if present in small quantity, may be removed by washing the strychnine residue twice with acetone, using 0·5 c.c. each time. W. P. S.

Estimation of Indigotin. WILLIAM THOMSON (*J. Soc. Dyers and Col.*, 1921, **37**, (6), 166—168).—A description of previous methods used for the estimation of indigotin is given. The author has devised a simplified process. One gram of the indigotin paste is dried on a watch glass, washed into a beaker with 30 c.c. of

ordinary sulphuric acid and heated at 50° for three hours. The product is cooled and diluted to one litre. Of this solution, 200 c.c. are diluted to one litre in a porcelain dish and titrated with an $N/50$-potassium permanganate solution until the liquid acquires a golden-yellow colour and shows a rim faintly tinged with pink. It is not strictly necessary to dry when 1 gram of indigotin paste is used, but an error of -0.3% occurs when 5 grams of undried paste are used for the sulphonation. It is important to use the same kind of illumination during the titration. When daylight and artificial light are used an error of 0.87% may occur. The presence of starch and glycerol (100% on weight of dry indigotin) leads to low results by Rawson's disulphonate and Bloxam's tetrasulphonate processes, but does not affect seriously the method now described. If, however, sulphonation is carried out at 90°, a dirty coloured solution is obtained and the end point cannot be determined within less than 8—10 drops. A. J. H.

Modification of the van Slyke Method of Protein Analysis. PAUL MENAUL (*J. Biol. Chem.*, 1921, **46**, 351—352).—Instead of precipitating the humin with calcium oxide, the former, ammonia, and some hexone bases are precipitated with phosphotungstic acid, and the phosphotungstates of the hexone bases dissolved by boiling. In the insoluble phosphotungstate, the ammonia is determined by distillation from alkaline solution, and the humin by a Kjeldahl determination of the residue, or better of the precipitate formed by adding sodium tungstate to an aliquot portion of the original hydrolysate. G. B.

Errors in the Detection of Albumin in Urine. E. RENAUX (*J. Pharm. Belg.*, 1921, **3**, 90; from *Chem. Zentr.*, 1921, ii, 869—870).—The presence of quinine can lead to the indication by Esbach's reagent of too high an albumin content. On the other hand the biuret test and the reactions with nitric acid, ammonium sulphate, and potassium ferrocyanide in acetic acid solution are rendered less sensitive. Sugar in urine must always be estimated by the use of Fehling's solution, since polarimetric estimations may be vitiated by the presence of lævulose. G. W. R.

Detection of Blood in Fæces. P. N. VAN ECK (*Pharm. Weekblad*, 1921, **58**, 723—727).—It has been shown (A., 1920 ii, 340) that a positive result with Adler's benzidine reaction does not necessarily denote the presence of blood. Evidence in confirmation of this conclusion is now adduced. W. J. W.

Estimation of Bilirubin in Blood Serum. G. HASELHORST (*Münch. med. Woch.*, 1921, **68**, 174—177; from *Physiol. Abstr.*, 1921, **6**, 130).—A colorimetric method of estimating the bilirubin content of 5 c.c. of venous blood. After separation of the corpuscles, the serum proteins are precipitated with alcohol. Bilirubin present then gives a violet-red coloration with Ehrlich's diazo-reagent. This may be compared with a Bordeaux red standard. E. S.

General and Physical Chemistry.

The Summation Method of Molecular Refraction, Particularly in the Case of Aromatic Hydrocarbons. A. L. VON STEIGER (*Ber.*, 1921, **54**, [*B*], 1381—1393).—Brühl's method of calculating the molecular refraction of organic substances is not completely satisfactory, since the results thereby obtained only agree approximately with the experimental values, whilst it also involves the effect of atomic and constitutive influences in a manner which cannot readily be justified from the physical point of view. The author has therefore applied to the calculation of molecular refraction the same considerations as were recently employed in calculating heats of combustion, definite refraction constants being assigned to the different bonds between the atoms [linking refraction constants], instead of to the separate atoms. A very satisfactory agreement is thus obtained between the calculated and experimental values, and it appears justifiable to conclude that all C–C and all C–H linkings in aromatic hydrocarbons are equivalent among themselves, but different from the corresponding values in the aliphatic series from the optical as well as from the thermochemical point of view. H. W.

The Influence of Constitution on the Dispersive Power of Optically Active Substances. XIII. [The Absorption Spectra of Optically Active Substances. H. RUPE, ALFRED KRETHLOW and KARL LANGBEIN (*Annalen*, 1921, **423**, 324—342. Compare A., 1911, ii, 450; 1912, ii, 1020; 1917, ii, 435).—In order to ascertain whether the phenomenon of anomalous rotation-dispersion is connected with the presence in the visible or in the near ultra-violet of an absorption band, the authors record the absorption curves for a number of optically active substances the rotation-dispersions of which are already known. The general conclusion drawn is that no such connexion can be substantiated.

The evidence on which this inference is drawn is as follows. Whilst it is true that *l*-menthyl acetoacetate, *l*-menthyl αα-diethylacetoacetate, *l*-menthyl benzoylacetate, ethyl camphorylideneacetate, $C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}CH{\cdot}CO_2Et\end{matrix}$, camphorylacetic acid, $C_8H_{14}<\begin{matrix}CO\\ |\\ CH{\cdot}CH_2{\cdot}CO_2H\end{matrix}$, and 1 : 2 : 2 : 3-tetramethyl-1-methanol*cyclo*pentane exhibit both anomalous rotation dispersion and either slight or pronounced selective absorption, *l*-menthyl diacetoacetate, α-benzhydrylacetoacetate, α-benzylideneacetoacetate, α-benzylidenebenzoylacetate, α-benzoylphenylacetate, and pyruvate, and also 3-benzoyl-1 : 2 : 2 : 3-tetramethyl*cyclo*pentane, all of which show anomalous rotation dispersion, as well as camphorylideneacetone, $C_8H_{14}<\begin{matrix}CO\\ |\\ C{:}CH{\cdot}COMe\end{matrix}$, and *l*-menthyl α-benzylacetoacetate, in which cases the anomaly is

somewhat doubtful, are all devoid of any noteworthy degree of selective absorption; on the other hand, camphorylidenebenzylideneacetone, $C_8H_4<\begin{matrix}CO\\ |\\ C{:}CH{\cdot}CO{\cdot}CH{:}CHPh\end{matrix}$, and *l*-menthyl α-styrylbenzoylacetate show no anomalous rotation dispersion, but possess marked selective absorption. Clearly, therefore, the two phenomena occur independently of one another, at least in the main. C. K. I.

Mass Spectra of Chemical Elements. III. F. W. ASTON (*Phil. Mag.*, 1921, [vi], **42**, 140—144. Compare A., 1920, ii, 344, 718).—The elements selenium, tellurium, iodine, antimony, and tin have been examined. Hydrogen selenide, tellurium methyl, methyl iodide, antimony hydride, and tin tetrachloride were used. No isotopes were found with any of these elements, although only the result with iodine is regarded as satisfactory. This is simple and of atomic weight 127. The work on xenon was repeated; trustworthy results were obtained for the five isotopes 129, 131, 132, 134, and 136, and two additional possible ones, 128 and 130, were discovered. Negative mass spectra of chlorine are described which confirm previous results with that element. J. R. P.

The Quantitative Sensitiveness of the Spectra of Silicon in Molten Salts and Steels. A. DE GRAMONT (*Compt. rend.*, 1921, **173**, 13—17. Compare A., 1918, ii, 49).—Tables are given showing the rays which persist with decreasing amounts of silicon as silica in molten alkali carbonates and with decreasing amounts of silicon in steel. The ultimate rays of silicon in the former case are $\lambda =$ 2881·6, 2516·1, and possibly 2524·1, which are apparent when as little as 0·005% of silicon is present. In the case of steels, the ultimate rays of silicon have disappeared when the silicon content has dropped to 0·03%, the ray $\lambda = 2516{\cdot}1$ alone persisting with 0·05% of silicon. W. G.

Absorption and Series Spectra of Lead. J. C. McLENNAN and R. V. ZUMSTEIN (*Proc. Roy. Soc. Canada*, 1920, **14**, [iii], (9)).—Experiments were made to determine the absorption spectrum of non-luminous lead vapour. There is well-marked absorption at λλ 2833 and 2170 Å.U. The wave-length 2203·57 Å.U. was strongly enhanced in the spark spectrum. No absorption was observed either at 10291 Å.U. or at 10500 Å.U., indicated by the resonance and ionisation potentials, but it is probable that if any did occur it was masked by the strong radiation emitted by the furnace. An attempt was made to select wave-lengths which might belong to the series $n = (1{\cdot}5, S) - (m, P)$. It was not possible to select a series of wave-lengths which would fit exactly to a simple formula, but some regularities were noticed. The principal series, the sharp and diffuse subordinate series, and the enhanced series in the emission spectrum are considered. The line 2833·17 Å.U. is regarded as the first member of the series $n = (1{\cdot}5, S) - (2, p_2)$ and 2170·5 Å.U. as the first member of the real principal series $n = (1{\cdot}5, S) - (m, P)$. Besides λ 2203·57 Å.U., strongly enhanced

in the spark spectrum, two other wave-lengths were found, 1726·2 and 1555·8. J. R. P.

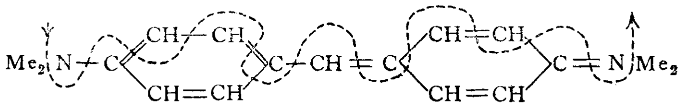
The Absorption Spectra of Europium and Samarium. WILHELM PRANDTL (*Zeitsch. anorg. Chem.*, 1921, **116**, 96—101).—The europium material used for previous experiments (A., 1920, ii, 721) has been again examined and subjected to further fractionation to separate it from the last traces of samarium, and it has been proved that the lines at λ 375 and 362, formerly attributed to samarium, are true europium lines. The europium line at λ 362 is much narrower and sharper than the samarium line in the same position. The absorption spectra of very pure specimens of europium and samarium nitrates have been photographed at concentrations ranging from 20 grams to 0·1 gram of the oxide per 100 c.c. Three new europium bands have been established, at 376·2—373·6, sharp on the red side, indistinct on the violet side, 367·2—365·5, very faint, and 363·7—361·7, very strong and sharp. Two new samarium lines were also discovered in the ultra-violet, at 355 and 345·5. The europium lines are in general much sharper than those of samarium. E. H. R.

The Principle of Combination and the Absorption Rays in *X*-Ray Spectra. A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 35—38).—An extension of previous work (this vol., ii, 421) in which the author shows that the ray β_7 of tungsten and the rare earths consists in reality of a doublet $\beta_7 = 733·5 \times 10^{-11}$ cm. and $\beta'_7 = 736·7 \times 10^{-11}$ cm. Further measurements of the rays γ_9, β_8, β_9, and $L\alpha_3$ are given. W. G.

The Electronic Structure of Heavy Atoms. L. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1921, **172**, 1650—1653).—A comparison of the physico-chemical indications concerning the electronic structure of the elements with the indications obtained from a study of their *X*-ray spectra. A recent spectrographic study (compare this vol., ii, 421) of the *L* series of uranium showed the absence of the *P*-ring. The anti-cathode was crystalline metallic uranium and the disappearance of the *P*-ring is explained on the hypothesis that the ions occupying the anticathodic focus must be in a very special state, in consequence of the very high local temperature existing there. This is borne out to some extent by recent work of Lilienfeld (compare *Physikal. Zeitsch.*, 1919, **20**, 280) and is similar to the hypothesis of Eddington with reference to the equilibrium of stars (compare *Scientia*, 1918, **23**). W. G.

Colour and Chemical Constitution. XII. Calculation of Colour from the Tautomeric Theory. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1921, **9**, 205—216. Compare this vol., ii, 365).—The additive colour relationships previously deduced are attributed to the motion of an electron, traversing with the velocity of light and in a sinuous orbit the series of alternate and double linkings, of which the connexion with depth of colour has been previously indicated by Hewitt and Mitchell (T., 1907, 91, 1251) and by Watson and Meek (T., 1915, 107, 1567). The application of this

conception to the case of aqueous solutions of Michler's hydrol is represented by the diagram:



Additive values (indicated in brackets) are assigned to the tautomeric systems ⁚C·CH⁚C⁚(103$\mu\mu$), ⁚C·CH⁚O(94$\mu\mu$), ⁚C·CH⁚NH(98$\mu\mu$), ⁚C⁚CH·NMe_2(126$\mu\mu$) and to the modifications caused by substitution. These values are successfully applied to the cases of dihydroxybenzhydrol, benzaurine, diaminobenzhydrol, Doebner's-violet, Michler's hydrol, malachite-green, sodium phenoxide, aniline, sodium *o*- and *p*-hydroxybenzaldehyde, the phthaleins, the naphthalene analogues of all these compounds, indigotin, hydroxyazobenzene (as quinonephenylhydrazone) and its sodium salt, and aminoazobenzene, and also to aurine, pararosaniline, and crystal-violet, which have hitherto occupied an exceptional position. The cases of auramine, fuchsoneimonium chloride, and its dimethyl derivative, and the higher azo-dyes, however, still await an adequate explanation. J. K.

Constitution and Colour. VII. Theory of Quinonoid Organic Onium Salts. F. KEHRMANN (*Helv. Chim. Acta*, 1921, **4**, 527—537. Compare A., 1918, i, 311).—A theoretical paper in which fresh experimental material is not brought forward. Arguments are adduced and examples given to show that it is impossible at present to eliminate the quinonoid formulæ for the majority of dye salts, and that these are the most satisfactory expressions until it is possible to do justice simultaneously to Werner's and the quinonoid theory. H. W.

Mechanism of Photochemical Processes. ALFRED COEHN and HEINRICH TRAMM (*Ber.*, 1921, **54**, [*B*], 1148—1151).—An examination of the influence of pressure and degree of desiccation on the explosibility of mixtures of carbon monoxide and oxygen has shown (1) that a moist mixture can be exploded by a spark at any pressure; (2) that a mixture, dried by short exposure to the action of solid carbon dioxide and alcohol, cannot be exploded but inflames and burns quietly, and (3) that a mixture which has been cooled for a sufficient time cannot be inflamed; a pale blue zone forms round the spark gap and slight combination is indicated by a small diminution of pressure. Exposure of mixtures belonging to the three types to ultra-violet rays of a quartz mercury lamp leads to practically the same result in each case, combination occurring to the extent of 4—5% within an hour. It follows, therefore, that the presence of aqueous vapour does not play a part in the union of carbon monoxide and oxygen under the influence of radiant energy. The reason of the markedly restrictive action of aqueous vapour on the decomposition of carbon dioxide in ultra-violet light is not to be found in the inability of carbon

monoxide and oxygen to combine on exposure to light in the absence of moisture. H. W.

The Photo-chemistry of Lead Compounds. CARL RENZ (*Zeitsch. anorg. Chem.*, 1921, **116**, 62—70).—Lead chloride darkens when exposed for a long time to intense light. The sensitiveness depends to some extent on the method of preparation; lead chloride crystallised from hot hydrochloric acid blackens relatively quickly. Dilute nitric acid does not remove the colour, and it appears that a lead photochloride is formed. When lead oxide is exposed to light under water, a partial reduction to metallic lead occurs, whilst the oxygen set free oxidises part of the lead oxide to peroxide, and this in turn combines with lead oxide to form plumbate. The metallic lead is reoxidised by air contained in the water. The formation of metallic lead was proved by exposing to light a mixture of lead oxide and lead chloride which had been boiled with hydrochloric acid. When the product was treated with dilute nitric acid, lead was dissolved with evolution of hydrogen and a slight residue of peroxide remained. There was no evidence of formation of oxychlorides of lead. It is suggested that compounds of the different lead isotopes may be differently affected by light, and the same may be the case with silver and thallium compounds. A possible method of separating isotopes is indicated. E. H. R.

The Catalytic Action of Electrolytes on the Photolysis of Eder's Solution. G. BERGER (*Rec. trav. chim.*, 1921, **40**, 387—393).—Previous experiments formed the basis of an hypothesis for the existence of a photochemical effect of electrolytes, of a catalytic nature, produced by the electrostatic forces of ions, in solutions in which reactions occur under the influence of light (compare A., 1920, ii, 725). Further experimental results taken in conjunction with the previous results indicate that the theories of Roloff (A., 1894, ii, 221) and Winther (A., 1909, ii, 283) do not offer an adequate explanation of the catalyses by salts in Eder's solution. The author prefers the theory of the existence of an effect of electrolytes, there being probably a relation between the forces producing this effect and the interionic forces of Miller (*Phil. Mag.*, 1912, [vi], **23**, 551), Hertz (A., 1912, ii, 120), and Bjerrum (A., 1919, ii, 9). W. G.

Photocatalysis. I. The Synthesis of Formaldehyde and Carbohydrates from Carbon Dioxide and Water. EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and WILLIAM FRANCIS BARKER (T., 1921, **119**, 1025—1035).

The Intensity of Reflection of *X*-Rays by Rock-salt. II. W. L. BRAGG, R. W. JAMES, and C. H. BOSANQUET (*Phil. Mag.*, 1921, [vi], **42**, 1—17. Compare *ibid.*, **41**, 309).—Experiments are described for the determination of the amplitude of the wave diffracted in various directions by the chlorine and sodium atoms when homogeneous X-rays of unit amplitude fall on these atoms in a crystal of rock-salt. The amplitude is expressed in terms of that diffracted

by a single electron. The results indicate the correct number of electrons in the atoms of sodium and chlorine. J. R. P.

Rutherford's Discovery of a New Light Atom Nucleus. ADOLF SMEKAL (*Naturwiss.*, 1921, **9**, 77—82, 93—98; from *Chem. Zentr.*, 1921, iii, 2—3. Compare A., 1920, ii, 541).—A discussion and criticism of Rutherford's discovery of the helium isotope X_3. G. W. R.

Probable Normal State of the Helium Atom. EDWIN C. KEMBLE (*Phil. Mag.*, 1921, [vi], **42**, 123—133).—The model of the helium atom proposed by Franck and Reiche (A., 1920, ii, 656) provides no explanation of the chemical properties of helium, gives the wrong ionisation potential, and does not harmonise with the observations of Fricke and Lyman (this vol., ii, 362) on the ultra-violet emission spectrum of helium. The facts regarding the excitation of the various lines in the arc spectrum of helium show that the only stationary states from which direct passage to the normal state is ordinarily possible are those from the series (m, S); that the direct transfer of atoms from the states (m, S) to the normal takes place with relative difficulty; and that the presence of some common impurity in helium provides an indirect path for the return of atoms to the normal state which is accompanied by the emission of more than one radiation frequency. The resulting angular momentum of the normal helium atom, on Bohr's theory, would be zero. Neither of two possible models having zèro angular momentum is very satisfactory, and it is possible that Bohr's principle applied to the atoms returning to the normal state may have to be abandoned. A symmetrical model with one unit of angular momentum is suggested as a possible solution of the problem. J. R. P.

Mobilities of Ions in Helium at High Pressure. J. C. MCLENNAN and E. EVANS (*Proc. Roy. Soc. Canada*, 1920, **14**, [iii], 19–26).—Pure helium at high pressures does not exhibit any appreciable metallic conductivity. The mobilities of positive and negative ions produced in helium at 81 atm. pressure by α-rays from polonium were found to be $2{\cdot}52 \times 10^{-2}$ and $4{\cdot}26 \times 10^{-2}$ cm. per sec. per volt per cm., respectively. They do not vary inversely with the pressure at high pressures. J. R. P.

A New Radioactive Substance in Uranium. OTTO HAHN (*Ber.*, 1921, **54**, [*B*], 1131—1142).—It is found that a new radioactive substance possessing the chemical properties of protoactinium is present in ordinary uranium salts. It emits β-radiations and has a half life period of six to seven hours. The radiations are highly complex; within the limits examined, the halving thickness increases from 0·014 to 0·12 mm. of aluminium. Under the prescribed conditions, the intensity of radiation of the new substance is only about 0·25% of that of uranium-X (uranium-X_1+ uranium-X_2) obtained from the same quantity of uranium. The parent substance can only be uranium-X_1 or a new uranium-X_1 isotope of similar life period. In the former case, uranium-X_1

suffers a dual degradation of a type which has not been observed previously among radio-elements. In the latter case it is probable that a new uranium degradation series exists which has a small intensity of radiation and the individual members of which can be arranged as isotopes in the known uranium–radium series. Until the parentage of the new substance is definitely established, the author proposes to designate it uranium-*Z*.

The substance is isolated in the following manner, since it is found that under the usual conditions uranium-*Z* invariably accompanies uranium-*X*. Enrichment in the latter is affected by a few fractional crystallisations of the uranium nitrate from water whereby the active materials remain in the mother-liquors. Iron chloride is added to the latter and the iron, carrying the uranium-*X* and uranium-*Z* with it, is precipitated by the addition of ammonia and ammonium carbonate. The iron precipitate is treated with a solution of tantalum in hydrofluoric acid, lanthanum nitrate is added, and the mixture is digested on the water-bath for a considerable time with dilute sulphuric and hydrofluoric acids. The lanthanum together with uranium-*X* is thereby precipitated as the insoluble fluoride. The filtrate is evaporated and the residue gently ignited, whereby the tantalum precipitate becomes insoluble in acid whilst the iron precipitate remains soluble. The latter is brought into solution by concentrated hydrochloric acid and the residue is warmed for some time with aqua regia and filtered after being diluted. The tantalum remains on the filter in a perfectly colourless condition. Uranium-*Z* remains almost completely with the tantalum, only small quantities being generally found with the iron precipitate; both, however, retain small amounts of uranium-*X*, which, however, can be almost completely eliminated by a second treatment of the iron-tantalum solution with lanthanum nitrate. It is thus possible to obtain specimens of uranium-*Z* which are 99·5% radioactively pure, only about 0·5% of the activity being due to uranium-*X*. H. W.

Origin of Uranium-Z_2 (Uranium-*Z*). M. C. NEUBURGER (*Naturwiss.*, 1921, **9**, 235—236; from *Chem. Zentr.*, 1921, i, 1015).—Supplementary to the work of Hahn (see preceding abstract), the author describes three possible types of disintegration in the radium–uranium series to account for the occurrence of the newly-discovered uranium-*Z*. The existence of two new elements thereby follows, namely, uranium III in Group VI, giving α-rays, and uranium-*Z* in Group IV, giving β-rays. Besides the transformations due to the emission of ordinary α-rays, there are others due to Rutherford's helium isotope, X_3, which are termed *iso*-α-particles.
G. W. R.

Origin of Uranium-*Z*. OTTO HAHN (*Naturwiss.*, 1921, **9**, 236; from *Chem. Zentr.*, 1921, i, 1015).—The author rejects the possibility of the transformations suggested by Neuburger (preceding abstract) as improbable and lacking experimental foundation.
G. W. R.

Thermal and Electric Conductivities of Metals. WALTHER MEISSNER (*Jahrb. Radioaktiv. Elektronik*, 1920, **17**, 229—273).—A summary of recent work on the subject. J. R. P.

Electrical Conductivity in Solid Crystallised Compounds. III. The Electrical Conductivity of Silver Sulphide and Cuprous Sulphide. C. TUBANDT, SOPHIE EGGERT, and GUSTAV SCHIBBE (*Zeitsch. anorg. Chem.*, 1921, **117**, 1—47).—The methods described in previous papers (A., 1920, ii, 279; this vol., ii, 426) have been used for the investigation of the electrical conductivity of silver sulphide and cuprous sulphide, to settle the debated question whether these are metallic or electrolytic conductors. The conduction of silver sulphide between metallic electrodes is interfered with by the rapid growth of a metallic bridge between the electrodes. This difficulty was overcome, as in previous work, by interposing between the small cylinder of silver sulphide and the platinum cathode a cylinder of silver iodide, using a silver anode. The α-form of silver sulphide, stable above 179°, was found to be a pure electrolytic conductor, following Faraday's law perfectly. The current is carried entirely by the silver ions with the high migration velocity of 0·11 cm. per sec. The form of silver sulphide stable below 179°, however, was found to be a mixed conductor, about 80% of the current being carried by the silver kations, the remainder being conveyed as in a metallic conductor. For the ingenious experimental method by which this result was obtained, the original must be consulted. The proportion of the current carried electrolytically is influenced to some extent by the presence of impurities in the silver sulphide, by the temperature, and by the current strength. The lower limit of temperature for the experiments was 145°, the transition point of silver iodide, since only the cubic form of this substance is effective in preventing metallic short-circuiting. The proportion of metallic conduction was found to increase with falling temperature and with increasing current strength.

Only the high temperature form of cuprous iodide could be investigated, as its transition point, 91°, is below that of silver iodide. After many experimental difficulties had been overcome, it was shown that the cubic form of cuprous iodide is a pure electrolytic conductor, the current being carried solely by the cupro-ions. E. H. R.

Electrical Conductivity in Solid Crystallised Compounds. IV. The Electrical Conductivity of Solid Silver Sulphide–Silver Mixtures. C. TUBANDT and SOPHIE EGGERT (*Zeitsch. anorg. Chem.*, 1921, **117**, 48—58).—When a current is passed through a solid cylinder of a mixture of silver sulphide and silver, using a silver anode and platinum cathode with a cylinder of silver iodide between the cathode and the solid electrolyte (compare preceding abstract) above 179°, the amount of silver dissolved from the anode is not in agreement with Faraday's law, although at this temperature silver sulphide is a pure electrolytic conductor. It is found, however, that if the electrolysis is continued for a

sufficient length of time, the whole of the silver in the silver sulphide gradually wanders to the cathode, leaving eventually pure silver sulphide which then behaves as a pure electrolytic conductor. This phenomenon can be utilised to free silver sulphide from silver, and also provides a method of proving the formation of a silver bridge when silver sulphide is electrolysed between metal electrodes. It also verifies the results of other workers that silver and silver sulphide do not form mixed crystals, but a coarse mechanical mixture. The experiments were made with mixtures containing up to about 13·5% of silver. E. H. R.

Electrical Conductivity and Density of Aqueous Solutions of Electrolytes. ADOLF HEYDWEILER (*Zeitsch. anorg. Chem.*, 1921, **116**, 42—44).—The results of conductivity and density measurements of aqueous solutions of about sixty metallic salts of inorganic and organic acids are given in tabular form.
E. H. R.

Influence of Forging on the Electrical Resistance of Steel. EUGÈNE L. DUPUY (*Compt. rend.*, 1921, **172**, 1660—1662).—When a bar of steel is drawn into wire the electrical resistance decreases as the section diminishes. During the wire-drawing the zones of perlite and ferrite distributed without orientation in the bar become aligned and elongated into filaments with a consequent diminution in the resistance. If such wire is heated to 800° and cooled at a suitable velocity the alignment disappears and the micrographic structure becomes similar to that of the original bar. The variation in the resistance, however, persists although sensibly lessened. It is shown that the wire contains, even after annealing, iron oxide in solution and a part of the resistance of the metal is due to the presence of this oxide. W. G.

Overvoltage. I. A Comparison of the Methods of Determination, especially as Applied to the Mercury Cathode. SYDNEY DUNNILL (T., 1921, **119**, 1081—1088).

Nature of Chemical Forces and the Anomaly of Strong Electrolytes. WILLIAM HUGHES (*Phil. Mag.*, 1921, [vi], **42**, 134—138).—On the assumption that interionic forces in solutions of electrolytes are inverse-square functions of the distances apart of dissimilar ions, and that the forces causing dissociation of molecules are inverse higher power functions of the distance, a quantitative theoretical interpretation of the Rudolphi dilution law and a qualitative interpretation of the van't Hoff dilution law are given. J. R. P.

The Theory of Electrolytic Ions. XXII. The Migration Velocity of some Ions. A Second Test of Paul Hertz's Theory of Ion Conductivity. RICHARD LORENZ and WILHELM NEU (*Zeitsch. anorg. Chem.*, 1921, **116**, 45—61).—Applying von Laue's theory of ionic mobility (A., 1916, ii, 289) an experimental method was devised for measuring the velocity of migration of ions by measuring the displacement of the surface separating two

solutions, one of which contained a coloured ion to serve as indicator, when electrolysed. Measurements were made at 18° and 25°, at dilutions from 1/4 to 1/2048*N* for the MnO_4', BrO_3', IO_3', ClO_3', and F' ions. The relation between ionic mobility and concentration, in all cases except that of the iodate ions, which gave abnormal results, confirmed the applicability of Hertz's theory of ionic conductivity. The value of Hertz's *A*-constant found was 9·1 at 18°, which agrees with that found by Lorenz and Osswald from measurements of the conductivity of sodium acetate (this vol., ii, 158), but does not correspond with the theoretical value, 18·9. No conclusion could be drawn from the experiments regarding the completeness of dissociation of strong electrolytes. E. H. R.

The Theory of Electrolytic Ions. XXIII. The Conductivity of some Binary Electrolytes. Third Test of Paul Hertz's Theory of Conductivity. RICHARD LORENZ and WILHELM MICHAEL (*Zeitsch. anorg. Chem.*, 1921, **116**, 161—182).—The electrical conductivities of potassium permanganate, potassium chloride, sodium chloride, sodium bromide, and potassium bromide were redetermined at 25° at dilutions from 1/8 to 1/2048*N*. The ion mobilities were calculated, making use of the direct determination of the mobility of the MnO_4' ion by Lorenz and Neu (preceding abstract). The greater part of the paper is devoted to a discussion of the Hertz function (compare this vol., ii, 158, and A., 1912, ii, 120) and to the development of a graphic method for calculating the constants of the Hertz formula. The values obtained for Hertz's so-called universal constant, calculated from the ionic mobilities found in the present series of experiments, confirm the conclusion that the constant is not universal, but has a particular value for each ion. Experimental errors may affect seriously the values found for the constant, but such errors are not likely to cause variations so large as those actually observed. E. H. R.

The Theory of Electrolytic Ions. XXIV. The Conductivity of some Neutral Sodium Salts of Polybasic Organic Acids. RICHARD LORENZ and A. SCHEUERMANN (*Zeitsch. anorg. Chem.*, 1921, **117**, 121—139).—The molecular conductivities of the neutral sodium salts of oxalic, malonic, succinic, benzoic, phthalic, *iso*phthalic, terephthalic, pyromellitic, and mellitic acids at 25° for a wide range of dilutions were measured, with the object of determining how the different stages of dissociation would affect the conductivity with increasing dilution. When the conductivities as ordinates were plotted against $\sqrt[3]{c}$, where *c* is the concentration, the curves obtained in the case of salts of mono- and di-basic acids were approximately straight lines between the concentrations 1/1024 and 1/64, but at higher concentrations the curves were deflected upwards. The curves for salts of acids of higher basicity were not straight over any part of their course. In the case of salts of aliphatic dibasic acids, the part of the curve which is deflected when $\sqrt[3]{c}$ is used becomes straight if $\sqrt[4]{c}$ is chosen instead. A graphic method is described for determining the limiting con-

ductivity, which consists in plotting the conductivity against $\sqrt{c}$, $\sqrt[3]{c}$, and $\sqrt[4]{c}$ and determining the probable point of intersection of the curves thus obtained at zero concentration. E. H. R.

The Theory of Electrolytic Ions. XXV. The Apparent Size of the Anions of some Aliphatic and Aromatic Polycarboxylic Acids and of Benzene. RICHARD LORENZ and A SCHEUERMANN (*Zeitsch. anorg. Chem.*, 1921, **117**, 140—146).—The radii of anions of the arsinic acids and their salts, calculated by Stokes's law from the ionic mobilities and space-filling numbers (A., 1920, i, 897) were found to lie between the values found for the benzene radius by Debye and by Steiger (A., 1920, ii, 355). The ionic mobilities of the anions and hence their radii have now been calculated from conductivity measurements of the sodium salts of oxalic, malonic, succinic, benzoic, phthalic, *iso*phthalic, terephthalic, pyromellitic, and mellitic acids. In the series of dibasic aliphatic acids the ionic radius increases as the homologous series is ascended, whilst the mobility decreases. In the case of the aromatic anions, the radius increases with increasing number of carboxyl groups, and is greater the more symmetrical the molecule. The mobility v/σ, where v is the calculated mobility and σ the number of carboxyl groups, decreases as the number of atoms in the ion increases. The ionic radii all fall between the values for benzene given by Debye and Steiger respectively. The possible configurations of the aromatic anions are discussed. E. H. R.

Photoelectric Investigations with Salt Solutions. II and III. TORSTEN SWENSSON (*Arkiv Kem. Min. Geol.*, 1920, **7**, No. 25, 1—7. Compare A., 1920, ii, 409).—The author has made experiments with the object of ascertaining if the alteration of *E.M.F.* occasioned by the ultra-violet illumination of salt solutions may be due to the formation of hydrogen peroxide. The unimolecular character of the decomposition of hydrogen peroxide in water and in nickel sulphate solution (compare Tian, A., 1911, ii, 35; 1915, ii, 828; Henri and Wurmser, A., 1913, ii, 744, 819; Mathews and Curtis, A., 1914, ii, 255, 602) is confirmed. The decomposition is slower in nickel sulphate solution than in water, and in either case the position of equilibrium, if such is actually reached, corresponds with a very low concentration of the peroxide. With reference to Thiele's statement that hydrogen peroxide is formed by the illumination of water (A., 1908, ii, 79), the author finds that if this is the case the peroxide is not obtained in a proportion detectable chemically. As regards the velocity of decomposition of hydrogen peroxide in the dark, this is not increased by previous illumination of the salt solution, the rapid decomposition ending immediately the illumination ceases.

Measurement of the effect on the *E.M.F.* of a nickel sulphate and a potassium sulphate element produced by addition to the solutions of hydrogen peroxide shows that, even were the peroxide formed in a proportion not detectable analytically, it could not be the cause of the alteration in *E.M.F.* resulting from illumination.

The temperature in the author's experiments varied by $\pm 1°$,

but the effect of illumination is in the opposite sense to that of rise of temperature and also greatly exceeds that involved in a rise or fall of temperature of 1°. T. H. P.

Magnetism and Atomic Structure. O. von Auwers (*Jahrb. Radioaktiv. Elektronik.*, 1920, **17**, 181—229).—A summary of recent work on the magnetism of elements, compounds, and alloys, from the point of view of theories of atomic magnetism. J. R. P.

Relation between the Anomalous Dilatation and the Thermal Variation of Magnetisation of Ferromagnetic Substances. P. Chevenard (*Compt. rend.*, 1921, **172**, 1655—1657).—To interpret the action of temperature on the properties of ferromagnetic substances the author has previously formulated an hypothesis of a progressive and reversible transformation of a form α, stable at absolute zero, and an isomorphous form β, stable at high temperatures. At all temperatures, θ, the state of the substance can be characterised by the proportion, x, of the form α. It is now shown that the quantity x is sensibly proportional to the square of the magnetisation at saturation, I^2, in the whole of the temperature range below the Curie point. Further, it is admitted that $x=(V-V_\beta)/(V_\alpha-V_\beta)$ where V, V_α, and V_β are the specific volumes of ferronickel and its two components α and β respectively at any temperature. W. G.

Critical Energy Increment and Trouton's Rule. Eric K. Rideal (*Phil. Mag.*, 1921, [vi], **42**, 156—163).—The critical energy increment is an average value, and the equilibrium between molecules of any one species in various stages of activation is assumed to follow the energy curve of the surrounding radiation. Only in the case of " black " molecules is the curve complete. At the critical temperature the maximum number of molecules is activated for the reaction of condensation to a non-polymerised liquid. Since the latent heat of evaporation is given by $L=Nh\nu$, Trouton's constant is, on the above hypothesis, merely an approximate expression of Wien's displacement law $\lambda_m T$=const. The value of the constant calculated from radiation data agrees closely with experiment: $\lambda_m T_c=0{\cdot}28986$; $\nu=c/\lambda_m$; $\therefore$ $L=Nh\nu=NhcT_c/0{\cdot}28986=9{\cdot}866T_c$. J. R. P.

Number of Atoms and the Physical Behaviour of Organic Liquids. W. Herz (*Zeitsch. anorg. Chem.*, 1921, **116**, 250—254. Compare Jorissen, A., 1920, ii, 90).—It was shown by Groshans that, for organic liquids containing carbon, oxygen, and hydrogen, if n is the number of atoms, M the molecular weight, T_s the absolute boiling temperature, and d_s the density at the boiling point, $n=193M^2/T_s^2d_s$. Combining this equation with the relation $n=1{\cdot}1T_c/p_c$ (A., 1920, ii, 285) and Trouton's rule, it is shown that $M/T_s^2=0{\cdot}00077$. This relation is found to hold with approximate accuracy for a series of seventy-nine compounds with boiling points ranging between that of ethane ($T_s=187{\cdot}6$) and that of anthraquinone ($T_s=653$). Combining Groshans's equation with the relation $v_c=0{\cdot}0009n$, it is shown that $v_c=0{\cdot}1737M^2/T_s^2d_s$, or, combining the latter with

$M/T_s^2=0{\cdot}00077$, $v_c=1{\cdot}34\times10^{-4}M/d_s$. The values of v_c calculated from both these formulæ for a number of esters of fatty acids agree well with the observed values. The relation between specific heat, s, and critical data for the higher paraffins can be expressed by the equation $sM=2{\cdot}44T_c/p_c$. Relationships are also found between the molecular heats and the molecular refractions and heats of vaporisation respectively of the paraffins from pentane to decane. E. H. R.

Total Heat of Liquid Carbon Dioxides. C. FREWEN JENKIN and D. N. SHORTHOSE (*Proc. Roy. Soc.*, 1921, **99**, [*A*], 352—361).—In a previous paper (A., 1915, ii, 741) a curve giving the total heat of carbon dioxide was given which was based on the assumption that the value of C_v is constant and equal to 0·214. The present paper describes the determination of the total heat of carbon dioxide, the object being to check the earlier results. Measurements were made at 12° and 100° and at pressures 900, 1000, 1100, 1200, 1300, 1500, and 1800 lb./sq. in. The values have been calculated for every 5° from 0° to 100° for each pressure from a smooth curve drawn through the experimental values. The present work indicates that C_v is not constant, but the data obtained are insufficient for an accurate calculation of this value. J. F. S.

High Temperature Investigations. XIII. The Measurement of Vapour Pressures at High Temperatures and the Vapour Pressures of the Alkali Haloids. OTTO RUFF and SUSANNE MUGDAN (*Zeitsch. anorg. Chem.*, 1921, **117**, 147—171).—Experiments were made primarily to test the experimental method for the determination of vapour pressures at high temperatures described by Ruff and Bergdahl (A., 1919, ii, 265). It was found very important that the material of which the crucible is made should be adapted to the substance under examination. Only substances such as metals with high surface tension can be vaporised in carbon or graphite crucibles. For substances with small surface tensions, thick-walled, optically black vessels must be used, such as blackened quartz. For metals, the volume of the crucible should be not more than 0·2 c.c., whilst for salts and similar substances it should be about 0·6 to 0·7 c.c. The optical pyrometer should be directed on to the blackened vessel. If the substance has a heavy vapour which might interfere with the readings of the optical pyrometer, this must be guarded against by passing as rapid a current of gas as possible. The vapour pressures of arsenic, antimony, bismuth, and copper were redetermined in the light of new experience, and in all cases except that of arsenic the former results were confirmed. For arsenic, the former temperature readings were found to be 20—40° too low.

The vapour pressure curves of the haloids of the alkali metals were determined, with the exception of the fluorides, for which a suitable crucible material could not be found. In general the vapour pressure decreases with increasing atomic weight of the components, except in the case of the lithium salts. As the atomic weight of the alkali metal increases, the influence of the halogen

on the vapour pressure becomes less. The following boiling points at atmospheric pressure were found: lithium chloride, 1337°, bromide, 1265°, iodide, 1189°; sodium chloride, 1442°, bromide, 1396°, iodide, 1299°; potassium chloride, 1415°, bromide, 1388°, iodide, 1319°; rubidium chloride, 1388°, bromide, 1340°, iodide, 1304°; cæsium chloride, 1289°, bromide, 1297°, iodide, 1280°. From the data obtained, the heats of vaporisation and critical temperatures were calculated for the salts. The relation between vapour pressure and absolute temperature is in fair agreement with the Ramsay-Young rule for all the salts. E. H. R.

High Temperature Investigations. XIV. The Vapour Pressures of the Oxides of Silicon, Aluminium, Calcium, and Magnesium. OTTO RUFF and PAUL SCHMIDT (*Zeitsch. anorg. Chem.*, 1921, **117**, 172—190).—The experimental method described in a previous paper (A., 1919, ii, 265) was made use of in an attempt to determine the vapour pressures at high temperatures of silica, alumina, lime, and magnesia. With silica and alumina, satisfactory results were obtained, after many experiments, using a graphite crucible glazed with vanadium carbide, which melts at 2850°, and, when mixed with vanadium oxide, gives a fairly dense glaze resistant up to 2400°. The boiling points of silica and alumina at 760 mm. are both about 2210° to 2230°. Most of the experiments were made in an atmosphere of nitrogen, but the results obtained in a few cases in which argon was used indicated that nitrogen might have a disturbing influence, especially in the case of lime. The experiments with lime and magnesia were unsatisfactory, except at low pressures, on account of chemical action between the oxide and the crucible. The results indicated, however, that the boiling point of lime at 760 mm. is near 2850° and that of magnesia near 2800°. E. H. R.

Fused Salts and the Law of Corresponding States. RICHARD LORENZ and W. HERZ (*Zeitsch. anorg. Chem.*, 1921, **117**, 103—110).—In his work on the temperature coefficient of free molecular surface energy (A., 1917, ii, 69, 70, 71), Jaeger expresses the opinion that fused electrolytes do not follow the law of corresponding states. The authors contradict Jaeger's opinion from his own data. He gives the fusion points, T_e, for a large number of salts, and also the temperature, T_2, at which vapour begins to form with great rapidity. The latter temperature is below, but not far removed from, the boiling point. The ratio T_e/T_2 is found to be approximately constant for all the salts, the mean value being 0·74, whilst, by the law of corresponding states, the ratio of the melting to the boiling point is 0·68. It is concluded, therefore, that the law can be applied to fused salts, and accordingly the boiling points, T_s, of the salts were calculated from the melting points from the equation $T_e/T_s=0·68$. Jaeger also determined the relation between density and temperature for the fused salts, and by extrapolation from his results, the density, d_s, at the calculated boiling point was calculated. The ratio d_e/d_s was then calculated for the salts, and the mean value found was 0·864, the corresponding value for liquids which

follow the law of corresponding states being 0·855. The critical temperatures, critical densities, and densities at absolute zero of the salts were also calculated, assuming them to obey the same law.

E. H. R.

The Heats of Formation of Glucinum Oxide and Chloride. W. MIELENZ and H. VON WARTENBERG (*Zeitsch. anorg. Chem.*, 1921, **116**, 267—268).—The heat of formation of glucinum chloride was determined by the direct combination of the metal and chlorine, and was found to be 112·6±0·4% cal., whilst Pollak (T., 1904, **85**, 604) found 155 cal. by measuring the heat of solution of the metal in hydrochloric acid. The new figure is more probably correct, as it lies on a smooth curve obtained by plotting heats of formation against atomic weights in the series Gl, Mg, Ca, Sr, Ba. The heat of formation of glucinum oxide was also determined by direct combination in a bomb calorimeter and was found to be 135·9±0·9% cal. This value also falls on a smooth curve with the heats of formation of other oxides of the glucinum group. E. H. R.

A Linear Relation for certain Atomic Volumes. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1921, **117**, 84—90).—In a previous paper (this vol., ii, 437) it was shown that there is a linear relation between the densities of a large number of corresponding chlorine, bromine, and iodine compounds and those of the haloids of the alkali metals. It is now shown that this relationship is intimately connected with the position of the alkali metals and halogens in the periodic system on either side of the rare gases. Between the atomic volumes of argon, krypton, and xenon, on the one hand, and of chlorine, bromine, and iodine on the other, there is strict proportionality, in the sense that $A.V._{\text{Halogen}}=a\times A.V._{\text{Rare gas}}$, where $a=0{\cdot}8015$. The relation between the atomic volumes of the alkali metals and of the rare gases preceding them is also linear, the equation being $A.V._{\text{Alkali metal}}=a\times A.V._{\text{Rare gas}}+b$, where $a=1{\cdot}823$ and $b=-6{\cdot}10$. A similar relation holds for the elements silicon, germanium, and tin, preceding the rare gases, and titanium, zirconium, and cerium, following the rare gases, but for no other group of elements. The relation holds, therefore, only between elements having the electron valencies, 0, ±1, and ±4. The linear relation previously found between the molecular volumes of the alkali haloids is, therefore, an expression of their atomic structure. That a similar relation holds for more complex halogen compounds is probably due to the relatively large volume of the halogen atom compared with that of the rest of the molecule. There is a similar linear relation between the absolute boiling points of the halogens and of the rare gases. E. H. R.

Polymerisation in the Solid State; Polymerisation amongst Liquids. WILLIAM R. FIELDING (*Chem. News*, 1921, **122**, 13—17; 289—293; **123**, 1—5. Compare A., 1920, ii, 732).—The molecular weight is calculated from the formula $PWS=9$, where P=polymerisation factor, W=average atomic weight of the atoms composing the compound, S=specific heat. The formula is

applied to several solids and liquids. The results show that saturated hydrocarbons are highly but nearly equally polymerised near their boiling points; unsaturated hydrocarbons are less polymerised; the introduction of hydrogen into the benzene ring increases the polymerisation; the introduction of a side chain scarcely affects P; the introduction of halogens reduces P; on replacing one hydrogen atom in water by an organic radicle P is considerably increased, the increment due to CH_2 being approximately independent of temperature; *iso*alcohols are less polymerised than normal alcohols, but the two approach at the boiling point; the polymerisation of organic acids increases with the percentage of carbon and is less than that for the corresponding hydrocarbons; nitriles are slightly more polymerised than acids. J. R. P.

Surface Tension of Unimolecular Layers. A. MARCELIN (*Compt. rend.*, 1921, **173**, 38—41).—It has previously been shown (*Ann. Physique*, 1913) that any further quantity of oleic acid placed on water already covered with a layer of a thickness practically double that which corresponds with the maximum extension does not undergo spontaneous extension, but remains in the state of small or large globules: the layer may then be considered as saturated. Further measurements with oleic acid, *iso*butylborneol, and gum have confirmed this discontinuity. If the surface occupied by a given quantity of oleic acid is progressively reduced, the tension decreases and then suddenly becomes constant. The saturation pressure of the layer is the constant difference of surface tensions between pure water and water covered with a saturated layer.
W. G.

Properties and Molecular Structure of Thin Films of Palmitic Acid on Water. I. N. K. ADAM (*Proc. Roy. Soc.*, 1921, **99**, [*A*], 336—351).—A modification of the technique for examining the properties of thin films of substances on water is described, special attention being directed to the avoidance of leaks past the confining barriers and to correcting for the residual contamination on the water, which cannot be entirely avoided. The experiments on palmitic acid confirm, in general, Langmuir's results (A., 1917, ii, 525). The curves of compressibility of the films are accurately straight lines, except for a possible doubtful deviation at very low compressions. The properties of the film change abruptly at a hydrogen-ion concentration of $10^{-5}N$. The change is confined to films under compression less than about 16 dynes/sq. cm. The area occupied by each molecule becomes about 20% greater than on neutral solutions. Langmuir's view that the films consist of a single layer of molecules, orientated with their carboxyl groups toward the water, is confirmed and extended. Probably the hydrocarbon chains are tightly packed on neutral solutions, adjacent molecules being drawn into the water to different depths. On neutral solutions, the molecules rise in the water so that the carboxyl groups, which are probably of greater cross section than the chains, are in contact with each other. This arrangement gives a liquid film, whereas the packed hydrocarbon

chain normally gives a solid one. There is independent evidence of an increased attraction of water for carboxyl groups with increasing alkalinity. The formation of ionic micellæ of soap, as the film dissolves in the more alkaline liquids, is a simple consequence of the increased attraction on the carboxyl groups and the attractions of the chains for one another. Hysteresis in the unimolecular films of palmitic acid is absent, or extremely small in amount, at room temperature. Palmitic acid is completely insoluble in water, slightly on the acid side, of strict neutrality, and the films preserve their area and properties unchanged for hours. Compression beyond a certain point causes the films to collapse, the ejected molecules forming aggregates visible to the naked eye. The remainder of the film appears to be unchanged in properties. Different films and even different parts of the same film, vary very much in their resistance to collapse. The collapse appears to be aided by nuclei the nature of which can, at present, only be conjectured. J. F. S.

Viscosity and Molecular Dimensions of Gaseous Cyanogen. A. O. Rankine (*Proc. Roy. Soc.*, 1920, **99**, [*A*], 331—336).—The viscosity of gaseous cyanogen has been determined with the object of obtaining the data necessary to test the validity of the molecular structure of this gas put forward by Lewis (A., 1916, ii, 310) and Langmuir (A., 1919, ii, 328), and also of testing the hypothesis put forward by the author with reference to the collisions of non-spherical gaseous molecules (this vol., ii, 192). The viscosity was measured with highly purified material by the method previously described (A., 1910, ii, 829). The experiments yield the results $\eta_{15^\circ}=0{\cdot}986\times10^{-4}$ C.G.S. units and $\eta_{100^\circ}=1{\cdot}264\times10^{-4}$ C.G.S. units, from which, assuming the validity of Sutherland's law for the variation of viscosity with temperature, the value of the Sutherland constant C is calculated to 280 and $\eta_0=0{\cdot}935\times10^{-4}$ C.G.S. This agrees remarkably with Graham's value of $0{\cdot}95\times10^{-4}$ obtained by transpiration experiments. Making use of the values of C and η_0 and using Chapman's formula (*Phil. Trans.*, 1916, **216**, 279), the mean area presented by the cyanogen molecule in the gaseous state in collisions is $\bar{A}=1{\cdot}31\times10^{-15}$ cm.^{2}, a value which is probably accurate to 2%. Making the assumptions of Lewis and Langmuir with regard to the similarity of the nitrogen and cyanogen molecules, the distance apart of the centres is calculated to $2d=2{\cdot}30\times10^{-8}$ cm., that is, the diameter of the outer electron shell of the cyanogen molecule is $2{\cdot}30\times10^{-8}$ cm., which is remarkably close to the diameter of the outer electron shell of bromine, which, according to Bragg, has the value $2{\cdot}35\times10^{-8}$ cm., an agreement which is demanded by the fact that potassium bromide and cyanide have nearly the same molecular volume. J. F. S.

New Stalagmometer or Guttameter. Friedrich Eschbaum (*Ber. Deut. pharm. Ges.*, 1921, **31**, 211—219).—In the estimation of the surface tension of liquids by the drop method it is essential that the velocity of outflow should not exceed fourteen to sixteen drops per minute; this has been generally secured by attaching to

the stalagmometer or guttameter a sufficient length of capillary glass tubing. The same effect can be more readily obtained by the following device. The instrument is provided at its upper end with a glass stopcock which only has a hole on one side. The barrel is provided with grooves which run parallel to its length and communicate with one another at the top and bottom; a portion of the surface remains smooth in order that the stopcock may be closed. By suitably turning the stopcock, the air in its passage to the top of the liquid can be caused to pass through any desired length of capillary and the rate of outflow of the liquid can be thereby accurately regulated.

A table is given for the calculation of guttameter estimations to stalagmometer measurements and for the correction of the reading of any guttameter to normal guttameter weights. For every increase of 1° in the atmospheric temperature the weight of the drop (guttameter) decreases by 0·25% and the number of drops (stalagmometer) increases by 0·25%. H. W.

The Sorption of Hydrogen by Amorphous Palladium. JAMES BRIERLEY FIRTH (T., 1921, **119**, 1120—1126).

The Sorption of Alcohol and Water by Animal Charcoal. JOHN DRIVER and JAMES BRIERLEY FIRTH (T., 1921, **119**, 1126—1131).

Adsorption by Powdered Metals. I. HANS VON EULER and ARVID HJ. HEDELIUS (*Arkiv Kem. Min. Geol.*, 1920, **7**, No. 31, 1—15).—By reducing silver chloride by means of zinc and water and subsequently eliminating the zinc from the precipitated silver, the authors have obtained quite pure silver in a very finely divided form. By shaking such silver with dilute silver nitrate or potassium chloride solutions of various concentrations and titrating the solutions before and after this treatment, the proportion of the dissolved salt adsorbed by the powdered metal is ascertained.

In the case of silver nitrate, the acidity of the solution remains unaltered, so that the ion NO_3' is adsorbed as well as the silver ion; this result is in moderately good agreement with the results of conductivity measurements of the solutions before and after the adsorption. The finely divided silver settles more rapidly in presence of silver nitrate than in pure water. During the adsorption of potassium chloride no alteration takes place in the acidity of the solution, but in this case the silver collects into aggregates similar to those of silver chloride.

Calculation of the number of silver ions adsorbed per gram of the powdered silver and of the surface presented by the metal and comparison of the result with the values derived by other investigators for the radius of the sphere of molecular action afford strong support for the supposition that the adsorbed ions form several molecular layers or a molecular space as suggested by Polānyi.

Attempts to employ the powdered silver in sedimentation experiments in silver nitrate solution resulted unsatisfactorily, presumably

owing to the lack of uniformity in the magnitude of the metallic particles. T. H. P.

Adsorption of Water by Powdery Substances. K. SCHERINGA (*Pharm. Weekblad*, 1921, **58**, 937—942).—To determine the adsorption of water at different vapour tensions by various substances, they were enclosed in a U-tube, of which the interior was coated with paraffin and closed by perforated corks. A current of air was then passed through sulphuric acid and drawn through the tube, and by this means any desired degree of humidity was obtained. Animal charcoal has a high adsorption even at low vapour pressures; no surface condensation takes place with 30% humidity. Salts such as potassium bromide, chlorate, and sulphate effect no appreciable adsorption in moderately dry air; no surface condensation is found below 60% humidity. Powdered marble or quartz are very slightly adsorbent in very moist air; on the other hand, sand has a high adsorption, and is therefore unsuitable for estimation of water in foodstuffs. W. J. W.

Adsorption and Solubility. G. GEORGIEVICS (*Kolloid Zeitsch.*, 1921, **28**, 253—254).—A criticism of a paper, under the same title, by Lundelius (A., 1920, ii, 358) in which the author directs attention to some previous work on the relationship between adsorption and the other properties of the solvent and the dissolved substance (A., 1912, ii, 236; 1913, ii, 561). Several other points on which the work of the author is at variance with that of Lundelius are mentioned and criticised. J. F. S.

Diffusion Velocity in Solid Gold–Silver Mixed Crystals and the Diffusion Coefficient of Gold in Silver at 870°. W. FRAENKEL and H. HOUBEN (*Zeitsch. anorg. Chem.*, 1921, **116**, 1—15).—For measuring the diffusion velocity of gold into silver, use was made of Tammann's discovery of limiting concentrations in mixed crystals. It was found that gold–silver mixed crystals containing up to 6·0 mol.-% of gold, when in contact with pure gold, were turned deep black in half an hour by ammonium sulphide solution; mixed crystals containing from 6·0 to 12·0 mol.-% of gold were, under the same conditions, turned bluish-black, whilst crystals richer in gold were not attacked at all by the reagent. The diffusion experiments were made by embedding a silver wire vertically in a block of gold and heating at 870° for varying periods. The rate of diffusion of the gold into the silver wire was observed by etching the cross sectional surface of the silver wire with ammonium sulphide and observing the rate of decrease of diameter of the two zones corresponding with 0—6 to 6—12 mol.-% of gold. Applying the diffusion law to the results obtained, the diffusion coefficient at 870° was found to be 0·000037 $cm.^2$/per day. E. H. R.

Correlation of Compound Formation, Ionisation, and Solubility in Solutions. Outline of a Modified Ionisation Theory. JAMES KENDALL (*Proc. Nat. Acad. Sci.*, 1921, **7**, 56—62).—A theoretical paper in which the experimental results obtained

by the author and his colleagues are correlated and critically discussed (see Kendall and Booge, A., 1918, ii, 37; Gibbons and Kendall, A., 1915, i, 80). It is shown that the hypotheses of Milner, Ghosh, and others fail to explain the anomaly of the ionisation of strong electrolytes because they, like the older hypotheses, ignore the rôle of the solvent in ionisation. Working with non-aqueous solvents, it is observed that the most significant factor of conducting solutions is that they are non-ideal. Two non-associated substances which are chemically inert one towards the other never give a conducting solution on mixing. Ionisation is consequently always accompanied by interactions between the solvent and dissolved substance. In systems of one variable radicle, for example, dimethylpyrone and acids of widely divergent character, it is shown that the extent and stability of the compound formation, as determined from freezing-point curves, increase as the ionisation tendency or electro-affinity of the variable radicle, X, of the acid HX became more negative. In systems of more than one variable radicle, for example, aldehydes of divergent character with various acids, it is shown that the compound formation is more extensive the more electro-positive the radicle, R, of the aldehyde R·CHO and the more electro-negative the radicle, X, of the acid HX. In systems of the type ester–acid the extent of the compound formation increased regularly as the radicles R and R′ of the ester RCO_2R' were more electro-positive or as the radicle X of the acid HX was more electro-negative. In systems of the type acid–acid the weaker acid HX functions as a base with regard to the stronger acid HY, the stability of the resultant salt being greater the greater the electro-affinity of the radicles X and Y. From these results and conductivity measurements of the various mixtures it is shown that compound formation and ionisation proceed in parallel. Where compound formation is slight, ionisation is inappreciable, as compound formation increases in extent and where compound formation is very marked ionisation is extensive. Applying these results to aqueous solutions shows that the same facts are true. Strong acids invariably give stable hydrates whilst in no single case of a weak acid is there any indication of hydrate formation.

On the basis of the foregoing, the author puts forward a modified ionisation hypothesis, on the assumption that ionisation is preceded by compound formation and is indeed a consequence of such combination. According to this view, ionisation in solutions is due to neither the solvent nor the dissolved substance alone, but to a combination between the two to form unstable complexes. It has been shown that whilst in simple molecules the two radicles are in general attracted to each other so strongly that no dissociation is observable, yet in complex additive compounds the attractive forces between the radicles are so diminished that disintegration of the complex into oppositely charged ions may readily occur. Union with another molecule promotes ionisation. As evidence in favour of this view the case of the mercuric salts is quoted: all highly ionised mercuric salts yield hydrates [for example,

$Hg(NO_3)_2,8H_2O$; $Hg(ClO_4)_2,6H_2O$; $HgF_2,2H_2O$] whilst all slightly ionised salts are non-hydrated.

The solubility of salts is also shown to run parallel with compound formation. The sulphates of sodium and potassium are exceedingly soluble in pure sulphuric acid, those of barium, calcium, and magnesium are decreasingly soluble, and those of nickel, iron, and copper are practically insoluble. With electro-negative metals the solubility becomes appreciable with mercury and extensive with silver. The solubilities of formates in formic acid follow exactly the same rule. Similarly, the solubility of hydroxides in water (ROH—HOH) follow the same rule. J. F. S.

An Arrangement of a Microscope for the Examination of Opaque Crystals. M. FRANÇOIS and CH. LORMAND (*Bull. Soc. chim.*, 1921, [iv], **29**, 366—374).—The arrangement consists of an ordinary microscope to the lower part of the objectives of which a small concave mirror, pierced with a hole, is fixed. A very small electric lamp with an S-filament is placed in the axis of the microscope, its light being rendered parallel by a small lens. The crystals to be examined are placed on a cover-slip, which in its turn is placed on an opaque disk on a microscope slide.

W. G.

Law of Constant Proportions and Crystalline Structure according to W. H. and W. L. Bragg. E. PERUCCA (*Gazzetta*, 1921, **51**, i, 255).—Quartaroli's reasoning (A., 1920, ii, 602) is based on the presumption that the most simple crystalline individual must be composed of a complete elementary cell, as figured by Quartaroli or by Bragg and Bragg. Such elementary cell, however, serves only to establish how the various atoms of the molecules are arranged and orientated in the crystal during its formation, and is not intended to represent a crystalline individual actually existing. The latter is constituted of a whole number of molecules in accordance with the law of constant proportions and with the sole condition that the atoms constituting these molecules show suitable mutual orientation and constitute at least one elementary crystalline group in the sense indicated by Bragg and Bragg.

T. H. P.

Dendritic Crystallisation and its Influence on the Strength of Metallic Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1921, **116**, 21—41).—A theoretical paper in which it is shown that the formation of dendritic crystals depends on the vectorial character of crystallisation velocity and on the rate of flow of heat from different parts of the surface of a polyhedral nuclear crystal in a crystallising system. When the rate of cooling, and consequently the velocity of crystallisation, is high, growth is inhibited at the crystal face but accelerated at the edges and corners, and dendritic forms result. The parts played in dendritic crystal formation by velocity and direction of cooling, heat of crystallisation, convection currents, heat conductivity, viscosity, and diffusion velocity are discussed. From the method of formation of dendritic crystals,

it follows that all the branches of a dendritic crystal have the same crystallographic orientation. This can be proved by etching tests on the surface of sections of alloys cut perpendicularly through a dendritic system. The extent of a unigranular dendritic system, for instance, in copper, cannot always be detected by etching. By subjecting the specimen to pressure, however, glide planes are revealed which establish the true boundaries of each unigranular dendrite. It is found in this way that the copper crystals are much larger than is indicated by the etching test. Since a dendritic system behaves as a single large crystal, it is to be expected that alloys crystallised in this way should have poor mechanical strength, as is actually the case. The improvement of mechanical strength by recrystallisation or working is due to the breaking up of the dendritic system, and the formation of much smaller, differently orientated crystals. E. H. R.

The Composition of Eutectics and the Limiting Members of Mixed Crystal Series. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1921, **116**, 206—208).—A criticism of a paper by Daeves (this vol., ii, 454) in which it was shown that the composition of eutectics and saturated mixed crystals can be expressed in molecular fractions which are frequently multiples of 1/8. These proportions cannot have any relation to the distribution of the constituent atoms in space lattices, as suggested by Daeves. E. H. R.

Photo-sensitiveness of Arsenic Trisulphide Sols. H. FREUNDLICH and A. NATHANSOHN (*Kolloid Zeitsch.*, 1920, **28**, 258—262).—It is shown that sols of arsenic trisulphide are photochemically active. They sensitise the oxidation of colour substances, such as eosin and malachite-green, in light. The formation of colloidal sulphur by illuminating arsenic trisulphide sols depends on this photochemical sensitisation, for the hydrogen sulphide which is set free by the hydrolysis of the arsenic trisulphide is oxidised to sulphur through the sensitising action of the trisulphide micellæ. Mixtures of arsenic sulphide sols and sulphur sols are, according to Odén, unstable, although both are negatively charged. Both sols are amicroscopic, but on mixing under an ultra-microscope it is seen that the micellæ speedily become much larger. Consequently, the mixture of the sols is more sensitive to electrolytes than the individual sols; the coagulation values of hydrochloric acid and aluminium nitrate are less than half that for pure arsenic sulphide sol and still smaller than that for pure sulphur sols. This instability depends probably on a mutual action of the sols on one another, since the arsenic sulphide sol contains in all probability hydrogen sulphide or a polysulphide as active electrolyte, whilst the colloidal sulphur contains pentathionic acid. Pentathionic acid and hydrogen sulphide in the presence of one another are unstable and react with the formation of sulphur. The reaction robs the micellæ of both sols of their active electrolytes and reduces the stability. The arsenic sulphide sol is more sensitive to electrolytes after·illumination because colloidal sulphur is formed in it, and colloidal sulphur which contains arsenic sulphide sol after

illumination exhibits a smaller coagulation value toward electrolytes, even in the dark. J. F. S.

Velocity of Coagulation of Hydrosols of Congo-rubin in the Presence of Carbamide and Sucrose. JOSEF REITSTÖTTER (*Kolloid Zeitsch.*, 1921, **28**, 268—269).—The velocity of coagulation of congo-rubin sols, which have been rendered more viscous by the addition of various stated amounts of carbamide or sucrose, has been determined. The method consists in adding to 1 c.c. of a congo-rubin sol $(9-a)$ c.c. of distilled water, a c.c. of a solution of either carbamide or sucrose of known concentration, and after keeping for sixty seconds adding 1 c.c. of $2N$-sodium chloride and noting the time required for the colour to change to a definite violet tint. The experiments show that for small increases in viscosity the velocity of coagulation decreases more rapidly than is to be expected from the increase in viscosity, intermediate increases in the viscosity give coagulation velocities approximately in keeping with the theory, whilst large increases in viscosity give a velocity of coagulation much greater than that demanded by the theory. When a coagulated blue congo-rubin sol containing carbamide, as above, is heated at 60°, it becomes red and on cooling to 18° and adding a further quantity of 1 c.c. of $2N$-sodium chloride it again coagulates, but much more rapidly than before. A further repetition of the process gives a still more rapid coagulation. The original solution before warming required fifty secs. for coagulation, after once warming thirty-two secs. were necessary and after twice warming twenty-two secs. J. F. S.

The Equilibria of Permutites. F. W. HISSCHEMÖLLER (*Rec. trav. chim.*, 1921, **40**, 394—432).—An examination of the transformations of a sodium permutite with ammonium chloride indicates the production of false equilibria (chemical hysteresis), which can be removed by repeated transformations at the ordinary temperature. The position of the real line of equilibrium is displaced by repeated transformations with warm solutions. By keeping the permutite for some time in the dry state, the positions of both the false and true equilibria change, and the hysteresis diminishes but does not disappear. With such a permutite that has been kept for some time, a single transformation with ammonium chloride results in the almost complete disappearance of the hysteresis. The position of the false and true equilibria is independent of the dilution and the size of the particles in the transformation sodium permutite $\rightleftharpoons$ ammonium permutite. An industrial permutite behaved like a laboratory preparation which had been kept for some time.

The transformation sodium permutite $\rightleftharpoons$ calcium permutite also showed hysteresis, which was not suppressed by a single transformation. The final states depend on the dilution, but agree only qualitatively with the formula of Rothmund and Kornfeld (A., 1918, ii, 315).

The last part of the paper contains a critical survey of other

work on this subject, and an explanation of the hysteresis is given based on the structure of mixed crystals. W. G.

Some Base Equilibria in Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. anorg. Chem.*, 1921, **116**, 16—20).—Experiments on basic exchange in permutite were made by shaking a known weight of pure sodium, potassium, or ammonium permutite with measured volumes of solutions of different salts of known concentration, and subsequently, by analysis of the final solution, determining how much of the positive ion of the salt had been taken up by the permutite. The salts employed included those of copper, magnesium, zinc, nickel, cobalt, aluminium, barium, strontium, calcium, thallium, silver, manganese, chromium, lead, rubidium, and uranyl. Since the reaction is ionic, comparison should be made only between those bases the permutites of which have dissociation constants or conductivities of the same order. According to conductivity, the permutites fall into three groups, those of the alkali metals, silver, and thallium, $50—90\times10^{-5}$, those of the alkaline earth metals, $9—11\times10^{-5}$, and the rest with very slight conductivities. In general, the equilibrium constants obtained from the above experiments fall into similar groups, with certain exceptions. Silver and thallium, in spite of the strong dissociation of their permutites, are almost entirely removed from solution, whilst nickel and cobalt remain in solution. Generally the higher the atomic weight of the metal, the more readily it is removed from solution by the permutite, but aluminium is an exception to this rule. E. H. R.

The Decomposition of Acid Salts of Dibasic Acids in Aqueous Solution, especially the Influence of Bases on the Amount of this Decomposition. TH. SABALITSCHKA and H. SCHRADER (*Zeitsch. anorg. Chem.*, 1921, **116**, 183—192. Compare A., 1920, i, 707).—If the decomposition of acid salts of dibasic acids into neutral salt and free acid, or, in other words, the partition of the base between the two acid groups, is governed only by the ratio of the two dissociation constants, it should be independent of the base. Experiments to test this point were made by dialysing aqueous solutions of sodium, ammonium, and aniline hydrogen sulphates, and determining the free acid in the diffusate. The amounts of free acid found in the diffusate were in the proportion 0·58 : 0·23 : 1·5 for the sodium, ammonium, and aniline salt respectively. The high value of the aniline salt can be accounted for by hydrolysis, but the difference between the sodium and ammonium salts can only be due to the influence of the base on the decomposition of the acid salt. Experiments in which aqueous solutions of the potassium and ammonium salts of succinic and α-camphoric acid were extracted with ether also showed that the amount of free acid present in such solutions was not independent of the base. E. H. R.

Chemico-kinetic Study of the Velocity of Reaction. M. PADOA (*Gazzetta*, 1921, **51**, i, 193—200).—The author has investigated

the course of the combination of chlorine with hydrogen in presence of traces of iodine, under the influence of white, green, blue, or violet light, and at 0°, 10°, 20°, 30°, and 40°. The results obtained confirm the variability of the temperature coefficient of the reaction with the wave-length of the light used (compare A., 1915, ii, 678, 719; 1916, ii, 508, 592). Further, with variation of the temperature from 0° to 40°, the velocity of the reaction increases continuously with white or green light, whereas with violet or blue light it is greater at 20° than at either 0° or 40°. The existence of such a maximum in the velocity of reaction has not previously been observed, although diminution of the velocity of reaction with rise of temperature occurs with the interaction of iodate and iodide (Skrabal and Weberitsch, A., 1914, ii, 187), with the decolorisation of triphenylfulgide in yellow light (A., 1916, ii, 508), and with the oxidation of nitric oxide (Wourtzel, A., 1920, ii, 173).

The present condition of the kinetic theory of the velocity of reaction is discussed, particularly as regards the developments introduced by Pratolongo (A., 1918, ii, 70) and by Stern and Volmer (A., 1920, ii, 461) and the explanations they suggest of the fall in the reaction velocity with rise of temperature.

T. H. P.

The Velocity of Reaction in Mixed Solvents. I. The Velocity of Saponification of Two Ethyl Esters in Ethyl Alcohol–Water Mixtures. ALBERT ERIC CASHMORE, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1921, **119**, 970—978).

Velocity of Hydrolysis of *p*-Nitrophenetole. A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 510—516).—The experiments described form a continuation of the author's work on the production of ethers from chloronitrobenzene and alkyl oxide (this vol., i, 413). Hydrolysis was effected by means of the calculated amount of potassium hydroxide in aqueous alcoholic solution at 70° and at the boiling point of the solution. The conditions with regard to concentration are chosen in such a manner that they are strictly comparable with those of the previous series. The course of the reaction is followed by the titration of aliquot portions of the mixture at definite intervals with $0{\cdot}1N$-nitric acid, congo- and phenolphthalein-paper being used as indicator (K_0- and Ph-titre). After two hundred hours about 60% of the ether is hydrolysed at 70°, about 40% at the boiling point of the solution. The percentage of nitrophenol present in the mixture at any instant can be calculated from the formula $4{\cdot}3[K_0-(Ph+2)]=\%$ nitrophenol. The gradual fall in the K_0 titre is due to the reduction of the nitrophenetole to the corresponding azoxy-derivative by the alkyl oxide and the percentage of azoxy-compound can be calculated from the formula $2{\cdot}87(23{\cdot}3-K_0)=\%$ azoxy. The constants of the reaction for the interval thirty to two hundred hours at 70° are nitrophenol $k_2=0{\cdot}43\times10^{-4}$ and azoxy-compound, $k_2=0{\cdot}014\times10^{-4}$ at 70° and for the interval twenty to one hundred and fifty hours are $k_2=1{\cdot}15\times10^{-4}$ for the nitrophenol

and $k_2=0·10\times10^{-4}$ for the azoxy-derivative at the boiling point of the solution. H. W.

Measurements of the Maximal Stability of Organic Compounds. I. HANS VON EULER and INGVAR LAURIN (*Arkiv Kem. Min. Geol.*, 1920, **7**, No. 30, 1—16).—Dilute aqueous solutions of ethyl acetate have been examined in order to ascertain the acidities for which the ester is most stable at given temperatures. The inactivation constant for saccharase (A., 1920, i, 506), k_C, is compared with the hydrolysis constant of the ester, k, at the maximal stability, the velocity constant of the hydrolysis at 69·3° and $p_H=5·1$ being taken as 4×10^{-6}. For saccharase ($p_H=4·5$), $k_C=6·6\times10^{-3}$, whilst for ethyl acetate (p_H=about 5), k=about 2×10^{-6}. The temperature at which saccharase, under these acidity conditions, is inactivated to the extent of one-half, is 59·3°, whilst the corresponding temperature for the hydrolysis of ethyl acetate is 150—200°. Hence, the stability of ethyl acetate in aqueous solution is of a far higher order of magnitude than that of saccharase, and the conclusion is drawn that the inactivation of saccharase is a different process from the hydrolysis of an ester.

The temperature coefficient of the inactivation of saccharase indicates a pronounced maximum of the stability for an acidity of about $p_H=4·5$ (*loc. cit.*). At the optimal stability, ethyl acetate is so stable that for $p_H=4·5$ the temperature coefficient of the hydrolysis cannot be determined, but when $p_H=3·3$, this coefficient between 80° and 90° only slightly exceeds the value at $p_H=1$. T. H. P.

Variations in the Catalytic Power of Electrosols of Platinum. A. DE GREGORIO ROCASOLANO (*Compt. rend.*, 1921, **173**, 41—43. Compare A., 1920, ii, 607).—Even in very short intervals of time the catalytic power of electrosols of platinum varies, the variations being much more intense in the non-stabilised than in the stabilised colloids. These variations in the catalytic power of the systems are attributed to incessant variations in the composition (concentration of oxygen) of the disperse particles, and the stabiliser acts in restraining this constant transformation. From certain electrical measurements, the author concludes that the electric charge of the colloidal system is not the seat of its catalytic power. W. G.

New Conceptions of Electrolytes. II. The Introduction of a Catalysis Coefficient in Hydrogen-ion Catalysis. ERLING SCHREINER (*Zeitsch. anorg. Chem.*, 1921, **116**, 102—116).—In catalytic reactions such as the hydrolysis of esters or the inversion of sucrose by acids, assuming complete dissociation and that only the hydrogen ions are active, the reaction velocity should be proportional to the concentration. Actually, however, the catalytic effect at higher concentrations is greater, and a similar accelerating effect is produced by the addition of neutral salts. It is shown that, by the introduction of a catalysis coefficient, f_k, this extra catalytic effect can be accounted for. The new coefficient is found to be the reciprocal of the conductivity–viscosity coefficient, f_μ, which

is the ordinary conductivity coefficient corrected for the viscosity of the electrolyte (compare this vol., ii, 425). The ratio v/C, where v is the reaction velocity and C the acid concentration, thus corrected to vf_{μ}/C, gives a very good constant in the hydrolysis of acetates by hydrochloric acid alone and in presence of neutral salts, in the inversion of sucrose, and in the keto $\rightarrow$ enol acetone transformation. The degree of dissociation of weaker acids, such as dichloroacetic or cyanoacetic acid, can be calculated from catalysis measurements, and the results agree very closely with those calculated from conductivity measurements. E. H. R.

Catalytic Decomposition of Hydrogen Peroxide. GÖSTA PHRAGMÉN (*Med. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 22, 1—13; from *Chem. Zentr.*, 1921, iii, 86—87).—The catalytic decomposition of alkaline, catalase-free hydrogen peroxide solutions was studied, varying the hydrogen-ion concentration by means of phosphoric acid and sodium hydroxide. The velocity of decomposition showed a slight maximum at P_{H} 11·8. The strongly alkaline, phosphate-free solution gave varying results even under identical conditions of experiment. The velocity of decomposition decreased both with increase and decrease of hydrogen-ion concentration, probably owing to the fact that the salt formed from hydrogen peroxide and sodium hydroxide is fairly stable and that only the free hydrogen peroxide takes part in the reaction. The velocity of reaction is not, however, purely a function of the hydrogen-peroxide concentration. A change was noted from a high rate of decomposition at P_{H} 9·9 to a negligible decomposition at P_{H} 8·6. The reaction is probably influenced by the presence of phosphate ions. Greater reaction velocities were obtained using ammonia and ammonium chloride solutions as buffer mixtures than in the case of the alkaline phosphate mixtures. The decomposition is almost completely inhibited by a potassium cyanide concentration of 0·0001, which may be attributed to a direct effect on the catalyst. G. W. R.

Velocity of Decomposition and Catalysis of Sodium Perborate. UMBERTO SBORGI and GIULIO NOCENTINI (*Gazzetta*, 1921, **51**, i, 289—307).—The authors have investigated the decomposition of sodium perborate in aqueous solution at various temperatures and find that at 10°, 20°, and especially 40° this decomposition does not follow any simple law, although it corresponds approximately with a unimolecular reaction; the values of K lie, however, on a regular curve which passes through a maximum. The decomposition products of the perborate influence the reaction, boric acid and sodium hydroxide having a retarding effect, which is due to mass action, and the metaborate a slight accelerating effect, which is more strictly catalytic. On the decomposition of the hydrogen peroxide originating by hydrolysis of the perborate, the above decomposition products as a whole exert an accelerating influence. The velocity of the decomposition at 20° is about double that at 10°, and that at 40° five to six times that at 20°. Tannin has no, and acetanilide but little, action on the decomposi-

tion, although both these compounds retard the decomposition of hydrogen peroxide considerably. Platinum, gold, and copper sheet, wire, or granules, and especially platinum-black, greatly accelerate the decomposition, and iron, nickel, and zinc retard it slightly, whilst some metals are without effect. Salts of iron, copper, lead, mercury and cobalt, sodium carbonate, etc., hasten the decomposition, which becomes almost instantaneous in presence of manganous sulphate; zinc, tin, and nickel salts act in the opposite way, cadmium salts cause enormous retardation, and aluminium, magnesium, and chromium salts are virtually without effect. As a rule, the catalytic effect of a salt is proportional to its concentration, but that of nickel sulphate passes through a maximum at a certain concentration. T. H. P.

Mutual Reaction of Oxalic Acid and Iodic Acid. II. Influence of Different Catalysts. GEORGES LEMOINE (*Compt. rend.*, 1921, **173**, 7—13. Compare this vol., ii, 108).—Platinum-black, spongy platinum, and charcoal from different sources were the catalysts examined, and of these platinum-black was by far the most active. In every case, the catalyst was relatively most effective at low temperatures and the effect increased with the weight of catalyst used and its fineness of division, but in neither case proportionately. The effect of gases previously occluded by the catalyst was examined, but no definite differences were established. W. G.

The Catalytic Oxidation of Alcohols under the Influence of Photoactive Ketones and the Explanation of the Phenomena of Catalysis. J. BÖESEKEN (*Rec. trav. chim.*, 1921, **40**, 433—445. Compare A., 1916, ii, 464; A., 1920, ii, 744).—Certain fresh experimental data in conjunction with previous work (*loc. cit.*, and Cohen, A., 1919, i, 124, 210; 1920, i, 393) are quoted as decisive proof of the theory of dislocation of catalysis, and based on it is given an explanation of the fundamentals of all catalytic phenomena. W. G.

Report of the Swiss Commission on Atomic Weights. A. L. BERNOULLI, P. DUTOIT, PH. A. GUYE, and W. D. TREADWELL (*Helv. Chim. Acta*, 1921, **4**, 449—458).—Owing to the peculiar position of Switzerland, the necessity for the consideration of a separate table of atomic weights arises from the fact that complete agreement does not exist between the data given by the International Committee of the American, British, and French Chemical Societies, and by the German Chemical Society. The main discrepancies occur in the cases of argon, nitrogen, boron, columbium, gallium, scandium, thorium, and yttrium. For the present, it is proposed to adopt those values for atomic weights which have not been revised by the International Committee since the 1916 report. In case where the figures have since been revised, they are only adopted in the following circumstances: (1) if the new and old values differ by 1/1000 to 1/10000 they must be obtained in a concordant manner by at least two different methods,

and (2) if differing by 1/1000 to 1/100 they must be derived as the concordant result of at least three different methods. H. W.

An Extraordinary Numerical Relationship between Calcium and Strontium. ALEXANDER SAKOSCHANSKY (*Chem. News*, 1921, **123**, 20).—If 0·11063 ($\log_{10}$ 1·290) be used as a multiplicand for atomic weights, it will give several pairs of corresponding values. J. R. P.

The Constitution of Molecular Compounds. PAUL PFEIFFER (*Zeitsch. angew. Chem.*, 1921, **34**, 350—354).—The aid afforded by the principles of isomorphism and substitution in studying the structure of molecular compounds, especially those in the labile form, is considered. The former principle is exemplified in a study of the constitution of complex platinum compounds (double chlorides, etc.), and the latter, in that of the neutral salts of amino-acids, and the quinhydrones. W. J. W.

Derivation of Acid Formulæ from a Law of Homopolar Atom Combination. HEINRICH REMY (*Zeitsch. anorg. Chem.*, 1921, **116**, 255—266).—The theory of Kossel (A., 1916, ii, 243), in which the formation of heteropolar combinations of atoms is accounted for in terms of the distribution of electrons in the valence spheres, does not account satisfactorily for homopolar compounds, in particular for the formation of acids from acid anhydrides. Sulphuric anhydride, for example, should be a completely saturated molecule. The hypothesis is now advanced that in such compounds the electrons which bring about the combination by transference, for example, from the sulphur to the oxygen atom, are not completely detached from the parent atom. The general tendency of every atom to surround itself with a group of eight electrons in its valence sphere again comes into play; six partly-detached electrons are already present, and there is therefore a tendency to combine with another oxygen atom to form the ion $SO_4^{\cdot\cdot}$. It is shown that in all co-ordinative saturated oxygen acids (ortho-acids) derived from elements in the five groups preceding the rare gases in the periodic system the central atom has the electron number 8, with the exception of the acids from boron, carbon, nitrogen, and aluminium, in which the central atom is surrounded by only six electrons. E. H. R.

Electrochemical Conceptions of Valency. JOHN ALBERT NEWTON FRIEND (T., 1921, **119**, 1040—1047).

New Forms of Soxhlet Extraction Apparatus. F. SIMION (*Chem. Zeit.*, 1921, **45**, 592).—One form of apparatus described is similar to an ordinary Soxhlet extractor, but the siphon is replaced by a U-shaped trap which delivers the condensed solvent back again into the extraction flask; the extraction thimble is supported in the cylindrical part of the apparatus; a tapped tube on one of the arms of the U-shaped trap allows portions of the solvent to be drawn off from time to time for examination. Another extractor consists of a wide tube having at its lower end a fairly wide stem,

the extraction thimble being supported in the wide tube. The vapours of the solvent rise through the stem, pass round the thimble, and up into the reflux apparatus, whilst the condenser solvent from the latter falls into the thimble and returns through the stem to the extraction flask.

OSKAR HAGEN (*ibid.*) discusses the advantages and disadvantages of these two pieces of apparatus. W. P. S.

Inorganic Chemistry.

The Reaction between Halogen Cyanides and Sodium Thiosulphate. ALBIN KURTENACKER (*Zeitsch. anorg. Chem.*, 1921, **116**, 243—249).—From the work of Meineke (A., 1893, ii, 246) and Dixon and Taylor (T., 1913, **103**, 974), it would appear that cyanogen bromide and iodide react differently with sodium thiosulphate. It is now shown, however, that there is no such difference. In neutral solution, the reaction may be represented by the equation $3CNBr+5S_2O_3''+H_2O=3Br'+2HCN+CNS'+SO_4''+2S_4O_6''$. In acid solution, the thiosulphate goes entirely into tetrathionate according to the equation $BrCN+2S_2O_3''+H^{\cdot}=Br'+HCN+S_4O_6''$. This is probably also the primary reaction in neutral solution, for during the reaction the solution becomes temporarily alkaline through the formation of sodium cyanide. The latter, however, reacts with tetrathionate according to the equation $3NaCN+Na_2S_4O_6+H_2O=NaCNS+Na_2SO_4+2HCN+Na_2S_2O_3$. The thiosulphate thus regenerated reacts further with halogen cyanide, and the net reaction is that represented by the first equation given above. E. H. R.

The Action of Cyanide on Tetrathionate. ALBIN KURTENACKER and ALBERT FRITSCH (*Zeitsch. anorg. Chem.*, 1921, **117**, 202—208).—Kurtenacker has shown (preceding abstract) that the tetrathionate produced in the reaction between halogen cyanide and sodium thiosulphate reacts with the sodium cyanide formed at the same time according to the following equation: $Na_2S_4O_6+3NaCN+H_2O=NaCNS+Na_2SO_4+Na_2S_2O_3+2HCN$. According to Gutman, however (A., 1906, i, 149), when the reaction is carried out in hot alkaline solution the products are thiocyanate, sulphate, and sulphite, whilst Mackenzie and Marshall (T., 1908, **93**, 1726) state that the same products are formed in the cold in absence of alkali. Further study of the reaction has now shown that it always proceeds primarily according to the above equation, with formation of thiosulphate. In presence of excess of cyanide, the thiosulphate can react further, with formation of sulphite and thiocyanate. This reaction, however, does not take place in dilute solution at the ordinary temperature, and only slowly and incompletely at

the boiling point. It only becomes quantitative in concentrated solution after long heating. On the formation of thiosulphate by the action of cyanide on tetrathionate is based an analytical method for determining the latter. To the neutral solution of the tetrathionate is added excess of potassium cyanide, the solution is acidified and the thiosulphate formed is titrated with iodine. One molecule of thiosulphate corresponds with one of tetrathionate.

E. H. R.

The Preparation of Selenic Acid. JULIUS MEYER and HANNS MOLDENHAUER (*Zeitsch. anorg. Chem.*, 1921, **116**, 193—200).—Selenic acid is reduced by hot hydrochloric acid to selenious acid with liberation of chlorine, but nevertheless chlorine can be used to oxidise selenious to selenic acid if the hydrochloric acid is removed as soon as it is formed. This was accomplished by passing a current of chlorine through a cold solution of selenious acid in concentrated nitric acid containing lead nitrate. The selenic acid formed separated as lead selenate, whilst the hydrochloric acid produced was reoxidised to chlorine. A more convenient and efficient method for the preparation of large quantities of selenic acid was based on the observation that selenium or selenious acid is oxidised completely to selenic acid by chloric acid. Selenium is first oxidised to selenious acid by heating with nitric acid. Rather more than the theoretical quantity of chloric acid, prepared from barium chlorate and sulphuric acid, avoiding excess of the latter, is added gradually, and the solution heated to expel chlorine and chlorine oxides. By concentrating in a vacuum, perchloric acid is removed, and a concentrated solution containing 85—90% of selenic acid is obtained, the yield being about 90—95% of the theoretical. By heating above 160°, selenic acid is slowly decomposed into oxygen and selenious acid. E. H. R.

Researches on Residual Affinity and Co-ordination. VI. Selenodithionic Acid and its Metallic Salts. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1921, **119**, 1066—1070).

The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia. EUGÈNE DECARRIÈRE (*Compt. rend.*, 1921, **172**, 1663—1666).—Small amounts of hydrogen, 0·44% by volume of the gaseous mixture, increase the activity of platinum as a catalyst in the oxidation of ammonia, whilst larger amounts, 1·0—1·5%, slightly lower the yield. The presence of hydrogen sulphide causes a progressive but not an absolute lessening of the activity of the catalyst. W. G.

Ammoniates as Binary Systems. I. FRITZ FRIEDRICHS (*Zeitsch. anorg. Chem.*, 1921, **116**, 141—160).—The three dimensional pressure–temperature–concentration curves for binary systems are discussed in detail for the following cases: (1) the components do not form a compound; (2) a compound is formed, (*a*) with a stable, (*b*) with a meta-stable melting point; (3) mixed crystals are formed, (*a*) in an unbroken series, (*b*) with a miscibility gap; (4) two liquid phases are formed. From a consideration of isothermal sections of

the three dimensional diagrams, which are pressure-concentration curves, it is shown that solubility relations can conveniently be investigated by measuring the equilibrium pressure at a comparatively small number of concentrations, when these are suitably chosen. An apparatus is described, designed to apply this tensimetric method to the investigation of ammonia systems at low temperatures down to $-50°$. E. H. R.

The Absorption of Oxides of Nitrogen by Nitric and Sulphuric Acids. A. SANFOURCHE (*Compt. rend.*, 1921, **172**, 1573—1576).—When nitric oxide and nitrogen peroxide, mixed in equimolecular proportions, act on sulphuric acid they do not behave like a simple mixture of the two gases, although this for the most part is what the gaseous mixture consists of. Although the proportion of nitrogen trioxide is small, its velocity of action is such that it serves as an intermediary in the solution, being reformed as fast as it is absorbed. This mechanism applies, not only to the absorption by sulphuric acid, but also to that by nitric acid, water, and alkalis. The two actions are (1) $NO+NO_2=N_2O_3$, (2) $N_2O_3+2H_2SO_4=2NO{\cdot}SO_4H+H_2O$. W. G.

The Distillation of Nitric Acids and of Mixtures of Sulphuric and Nitric Acids. PAUL PASCAL [with M. GARNIER] (*Ann. Chim.*, 1921, [ix], **15**, 253—290).—A more detailed account of work already published (A., 1917, ii, 569; 1920, ii, 162, 752). W. G.

Stability Relations of the Glass and Crystal Phases of Silicon Dioxide. RUDOLF WIETZEL (*Zeitsch. anorg. Chem.*, 1921, **116**, 71—95).—The heats of crystallisation of quartz, cristobalite, and chalcedony were determined by measuring their heats of solution and that of quartz glass in hydrofluoric acid and subtracting the former from the latter. Quartz and chalcedony gave the same value, about 2·2 cal. per mol., whilst that of cristobalite was lower, about 0·6 cal. per mol. The mean specific heats of these substances were also determined between normal temperature and their melting points. At high and low temperatures, quartz glass has the greatest specific heat, as it should have, being the modification stable at the higher temperature, but over a wide range it has a lower specific heat than quartz and cristobalite, and below 575° cristobalite has a lower specific heat than quartz. Variations in the transition temperatures and in the corresponding heats of transformation in the case of quartz and cristobalite were found to depend on the state of division of the material. With very finely-divided quartz the transition point was scarcely to be detected. It is concluded that chalcedony is not a distinct form of silica, but microcrystalline quartz. The melting point of cristobalite was found to be 1696°. Quartz can be melted without conversion into cristobalite; its melting point is between 1600° and 1670°.

To construct the energy (A–U) diagrams for the different phases of silica, by application of Nernst's heat law, the specific heats

of quartz, cristobalite, and quartz glass were determined at very low temperatures, down to about 18° abs. The calculated *A–U* diagram for the cristobalite–quartz transition agreed completely with the observations, the meta-stable transition point being at 1400°. E. H. R.

Some Unsaturated Silicon Compounds. HANS KAUTSKY (*Zeitsch. anorg. Chem.*, 1921, **117**, 209—242).—The unstable substance first obtained by Wöhler by the action of cold hydrochloric acid on calcium silicide has been further investigated. Two compounds of different stages of oxidation, between calcium silicide and silica, have been isolated. By carefully treating the silicide with cold dilute alcoholic hydrochloric acid in the dark, a white, solid substance was obtained, its formation being accompanied by evolution of hydrogen. It is spontaneously inflammable in air. Its composition corresponds with the formula Si_2H_2O, and its properties indicate the constitution $Si_2H{\cdot}OH$. It has been called *oxydisilin*. It is a powerful reducing agent, and can be oxidised quantitatively by means of bromine to silical bromide, Si_2OHBr, the term *silical* being used to signify the radicle Si_2OH—. Silical bromide is hydrolysed by water to form *silical hydroxide*, a red compound, which combines with strong acids, such as hydrochloric, sulphuric, formic, or acetic, to form salts which are all yellow to red in colour. The silical compounds are all powerful reducing agents. They, as well as oxydisilin, are decomposed by alkalis with evolution of hydrogen and formation of silica.

Halogenated hydrocarbons such as carbon tetrachloride, chloroform, or ethyl iodide in presence of traces of water and under the influence of light oxidise oxydisilin to silical compounds. The reaction does not proceed in the dark, but is extremely sensitive to light.

It is remarkable that oxydisilin and the silical compounds prepared as described above retain the external crystalline form of the calcium silicide from which they are formed, and the same crystalline form persists when oxidation is carried to the final stage, silica. That the substances have a very open structure is shown by the rapidity with which reactions proceed in the solid state, and also by the marked absorption of basic dyes by the end-product, silica. Rapid oxidation of the silical compounds, for example, by permanganate, is accompanied by the phenomenon of chemi-luminescence in a remarkable degree.

The unsaturated character of these compounds cannot yet be satisfactorily accounted for. The silical compounds may be of the oxonium salt type, and a certain similarity to some compounds of bivalent germanium suggests that the silicon in these compounds may be bivalent.

Silicalamino-compounds are formed by the action of anhydrous ammonia on the silical compounds, and from these, by the action of alcohols, liquid and solid organosilicon compounds are formed. These compounds belong to a higher stage of oxidation than the silical compounds. E. H. R.

Sodium Perborate. F. FOERSTER (*Zeitsch. angew. Chem.*, 1921, **34**, 354—355).—The composition of sodium perborate is more correctly represented by $NaBO_2,H_2O_2,3H_2O$ than by $NaBO_3,4H_2O$. When the salt, after dehydration at 50—55°, is further heated at 120° in a vacuum, it loses water, and the residue, which evolves oxygen on treating with water, consists chiefly of $(NaBO_2)_2O_2$ with some $NaBO_2,H_2O$ and metaborate. This compound, $(NaBO_2)_2O_2$, has properties which differ from those of $NaBO_3$, and this tends to imply the existence of a substitution product of hydrogen peroxide of the composition $ONa{\cdot}B{<}{\genfrac{}{}{0pt}{}{O}{O}}$, analogous to persulphates and percarbonates. This is confirmed by the fact that sodium perborate has been electrolytically prepared (Arndt., A., 1916, ii, 429). Sodium perborate, obtained by the action of hydrogen peroxide on the metaborate, behaves as the salt of an acid of greater strength than boric acid. W. J. W.

Colour of the Photochlorides and Colloidal Silver. I. KARL SCHAUM and HERMANN LANG (*Kolloid Zeitsch.*, 1921, **28**, 243—249).—The authors have prepared silver sols of different colours and examined the effect of the size of the particles and the distance between the particles on the optical behaviour of the sols. The colours of the photochlorides have been compared with those of the silver sols, and the silver haloid has been removed from the photo-haloid and the properties of the remaining silver examined. The silver sols are prepared from a nucleus sol in gelatin solutions to which is added definite quantities of a solution, *B*, consisting of 2 grams of sodium thiosulphate and 2 grams of *p*-phenylenediamine in 100 c.c. of water, and a definite quantity of a solution, *A*, consisting of 18 grams of sodium thiosulphate and 0·75 gram of silver nitrate in 100 c.c. of water, which is added very slowly. The nucleus sol is made from 10 c.c. of 10% yellow dextrin, 10 c.c. of 10% sodium hydroxide solution, 7·5 c.c. of 10% silver nitrate solution, and 22·5 c.c. of water, after keeping for thirty minutes, diluted to 1500 c.c. The preparation of the various sols is represented thus; the colours being for transmitted light.

	Colour.	Nucleus sol.	1% Gelatin.	Sol. *A*.	Sol. *B*.
I	orange-red	0·2 c.c.	9·2 c.c.	0·4 c.c.	0·2 c.c.
II	deep-red	5 c.c. of Sol. I	4·5 c.c.	0·2 c.c.	0·1 c.c.
III	deep reddish-orange	5 c.c. of Sol. II	4·5 c.c.	0·2 c.c.	0·1 c.c.
IV	dark red	5 c.c. of Sol. III	4·5 c.c.	0·2 c.c.	0·1 c.c.
V	purple	5 c.c. of Sol. IV	4·5 c.c.	0·2 c.c.	0·1 c.c.
VI	bluish-violet	5 c.c. of Sol. V	4·5 c.c.	0·2 c.c.	0·1 c.c.
VII	bluish-green	5 c.c. of Sol. VI	4·5 c.c.	0·2 c.c.	0·1 c.c.

The various sols become somewhat lighter in colour on dilution, and display the following colours by reflected light, I, practically colourless, II, blue, III, greyish-blue, IV, bluish-green—grey, V, greyish-green, VI, greyish-yellow, and VII, yellow. Treatment of the sols with reagents which dissolve silver such as photographic reducers and hydrogen peroxide does not cause the sols of small dispersity to pass through the above-named colour changes in the

reverse direction. Measurements of the diameter of the particles show that for transmitted colours the following diameters are associated with the following colours: yellowish-orange, $60\mu\mu$; orange-red, $90\mu\mu$; purple, $120\mu\mu$; violet, $150\mu\mu$, and bluish-green, $180\mu\mu$. J. F. S.

The Binary System, Ag_2S–Tl_2S. HANS HUBER (*Zeitsch. anorg. Chem.*, 1921, **116**, 139—140).—Equilibrium conditions in the silver sulphide–thallium sulphide system were investigated by the thermal method. The eutectic point is at 306° with 55% Tl_2S. When less than 31% of thallium sulphide is present, an arrest point is found at 358°, due to a reaction between the separated silver sulphide and the liquid phase, resulting in the formation of a crystalline compound, $4Ag_2S,Tl_2S$. Confirmation of the thermal data was obtained from the microscopical structure of the different mixtures. E. H. R.

Ammoniacal Silver Carbonate. DERVIN and OLMER (*Compt. rend.*, 1921, **172**, 1662—1663).—By repeated spontaneous evaporation in air of ammoniacal solutions of silver oxide, it was possible to obtain, after filtering off a small amount of metallic silver, crystals of ammoniacal silver carbonate, $Ag_2CO_3,4NH_3,H_2O$. Exposed to the air, these crystals lose water and ammonia, giving silver carbonate, which retains the shape of the original crystals. The ammoniacal carbonate blackens in sunlight. W. G.

The Solubility of Calcium Sulphide in Presence of Hydrogen Sulphide. E. H. RIESENFELD and H. FELD (*Zeitsch. anorg. Chem.*, 1921, **116**, 213—227).—The solubility of calcium sulphide in water is increased in presence of hydrogen sulphide, through the formation of calcium hydrosulphide. At 20°, the solubility of commercial calcium sulphide in water was found to be 0·212 gram per litre. Determinations were made of the solubility in presence of hydrogen sulphide at 0°, 20°, and 40° under pressures of the gas from 40 mm. to 760 mm. At 20° and 760 mm., the solubility, calculated as CaS, is 206·5 grams per litre. At pressures above about 200 mm., the relation between solubility and partial pressure of hydrogen sulphide can be expressed by a linear equation of the form $c=K_1+K_2p$ for each temperature, the values of K_1 and K_2 being, at 0°, 28·65 and 0·00499; at 20°, 25·17 and 0·00696, and at 40°, 23·10 and 0·00708. Over the whole range, the empirical equation $c=\sqrt{K_3 \log p}$ expresses the results with fair accuracy. Pure calcium sulphide can be prepared by extracting the crude material with aqueous hydrogen sulphide under pressure, in absence of air to avoid formation of polysulphide, and precipitating the pure calcium sulphide by removing the hydrogen sulphide from the solution at low pressure. E. H. R.

Colloidal Arsenates. II. Cadmium Arsenate Jellies. G. KLEMP and J. VON GYULAY (*Kolloid Zeitsch.*, 1921, **28**, 262—268. Compare A., 1915, ii, 256; 1918, ii, 200).—When solutions of dihydrogen potassium arsenate are added to solutions of cadmium

sulphate of appropriate concentrations, firm, transparent jellies are produced which cannot be poured from the vessel in which they are prepared. The same result is obtained when normal sodium arsenate which has been rendered neutral by the addition of acetic, hydrochloric, or arsenic acid is employed in place of the above-named salt. The jellies are not very stable, and on keeping for a short time become opalescent, whereon crystallisation sets in and the jelly becomes liquid. The crystals are very small and quite insoluble in water, as is also the gel, but both are readily soluble in dilute hydrochloric acid. The composition of the gel could not be determined because of its great instability. The crystalline salt has the composition $2Cd_3(AsO_4)_2,4CdHAsO_4,9H_2O$, and is to be regarded as a molecular mixture of tertiary and secondary arsenates. J. F. S.

A Hitherto Unknown Copper Aluminate of the Spinel Type. J. ARVID HEDVALL and JOSEF HEUBERGER (*Zeitsch. anorg. Chem.*, 1921, **116**, 137—138).—When cupric oxide and aluminium oxide are heated together, a reaction starts at about 700° and proceeds quickly between 750° and 850°. The product, which forms a chocolate coloured powder, has, when freed from unchanged oxides, the composition CuO,Al_2O_3, and is therefore of the spinel type. It is very resistant to solvents in general. When fused with potassium chloride, it undergoes partial decomposition, and the undecomposed portion crystallises on cooling in well-formed cubes and octahedra. E. H. R.

Ternary Aluminium Alloys. M. WAEHLERT (*Metall u. Erz*, 1921, **18**, 298—307).—The effect on the physical properties of aluminium of additions up to 10% of each of the following metals, copper, zinc, tin, and iron, was first investigated and the results were illustrated graphically. Copper and zinc increase the hardness and tensile strength but reduce the ductility, whilst tin has very little effect. The hardness, tensile strength, and elastic limit have been determined of the aluminium-rich ternary alloys with copper–zinc, copper–tin, and iron–zinc. The alloys of the first two series show a much smaller volume change on solidification than pure aluminium, and are in general harder and tougher but less ductile than the pure metal. Iron has a bad effect on zinc–aluminium alloys; it renders them hard, brittle, and difficult to pour (compare *J. Soc. Chem. Ind.*, 1921, 547A). A. R. P.

Reduction of Inorganic Haloids. I. Reduction with Aluminium and [the Preparation of] Aluminium-triarsenic Trichloride. OTTO RUFF and KARL STAIB (*Zeitsch. anorg. Chem.*, 1921, **117**, 191—201).—The catalytic action of aluminium chloride for inorganic reactions has been previously pointed out by Ruff (A., 1901, ii, 500; 1902, ii, 13). Arsenic trichloride can be reduced with yellow phosphorus in presence of aluminium chloride, forming a red compound sparingly soluble in arsenic trichloride. The same compound can be obtained in a purer form by heating together at 135—140° aluminium powder and arsenic trichloride with a

little aluminium chloride as catalyst. In absence of the catalyst, the reaction does not take place at all. The reaction takes place according to the equation $3AsCl_3+3Al=AlAs_3Cl_3+2AlCl_3$. Excess of aluminium chloride can be removed by extracting the product with hot arsenic trichloride, and after removal of the solvent by heating, the composition of the product agrees with the formula $AlAs_3Cl_3$. The oxidation equivalent, determined by treating the compound with concentrated sulphuric acid and titrating the sulphurous acid formed with iodine, was found to be 5, from which it follows that the compound contains only three principal valencies. The arsenic must therefore be regarded as held by co-ordination valencies. This view is supported by the fact that water decomposes the compound into aluminium chloride and black arsenic. Titanium tetrachloride and ammonia also decompose the compound, black arsenic being formed. It is stable in dry air, and when heated above 170° decomposes with formation of aluminium arsenide, arsenic, and arsenic trichloride thus: $AlAs_3Cl_3=AlAs+As+AsCl_3$. It is shown that aluminium arsenide and arsenic trichloride are also formed when black arsenic is heated with aluminium chloride at 120°. The new compound has d^{22} 2·85.

E. H. R.

Tervalent Manganese. JULIUS MEYER and ROBERT NERLICH (*Zeitsch. anorg. Chem.*, 1921, **116**, 117—136. Compare Meyer, A., 1913, ii, 599).—Experiments on the autoxidation of manganous compounds have led to the general conclusion that manganous hydroxide in suspension or in colloidal solution is oxidised by atmospheric air directly to manganese dioxide, whilst complex manganous salts in ammoniacal or alkaline solution are oxidised to manganic hydroxide. Manganous ions are not oxidised at all by atmospheric oxygen. The experiments were conducted by measuring the volume of oxygen absorbed by the manganous compound under specified conditions, and the results were confirmed by analysis of the products. Acceptors such as sodium sulphite or arsenite had no influence on the velocity or course of the reaction. Manganous hydroxide precipitated by sodium, potassium, calcium, or barium hydroxide gave in each case manganese dioxide, but a solution of manganous hydroxide in excess of ammonia in presence of ammonium chloride gave a precipitate of manganic hydroxide of a characteristic yellowish-brown colour. Potassium and sodium manganocyanides were oxidised to manganic hydroxide, whilst solutions of a manganous salt mixed with potassium thiocyanate were not oxidised at all.

In presence of tartaric or oxalic acid, manganous salts are not precipitated by alkalis, and autoxidation takes place rapidly. In presence of ammonia, the product is manganic hydroxide, but in presence of sodium or potassium hydroxide, manganese dioxide is formed, probably because in presence of these stronger alkalis the complex compound is less stable, some manganous hydroxide being always present and oxidising directly to the dioxide.

The oxidation by means of air of a solution of manganous chloride

made alkaline with ammonia, in presence of ammonium chloride, affords the most convenient method for preparing manganic hydroxide. The product is identical except in colour with that prepared by hydrolysis of potassium manganicyanide with water (*loc. cit.*), the darker colour of the latter being due to contamination with decomposition products of the cyanide. It is shown that acid hydrolysis of manganic salts leads to the formation of manganese dioxide and manganous salt, whilst alkaline hydrolysis merely precipitates manganic hydroxide. By acid hydrolysis, however, probably manganic hydroxide is first formed and at once decomposed, since it is shown that manganic hydroxide is decomposed by dilute mineral acids into manganese dioxide and manganous salt. That manganic hydroxide is a true tervalent manganese compound is probable from the fact that dilute hydrofluoric acid, hydrocyanic acid, and oxalic acid dissolve it completely, to form complex mangani-compounds. Concentrated sulphuric, selenic, phosphoric, hydrochloric, and hydrofluoric acids also dissolve it completely, but concentrated nitric acid oxidises it completely to manganese dioxide. Small traces of manganese can be detected by oxidising an ammoniacal solution of the mangano-salt with air, filtering, and treating the filter paper with a few drops of concentrated orthophosphoric acid. A reddish-violet colour is characteristic of manganese. This test is not interfered with by the presence of copper, ferrous and ferric iron, or cobalt. E. H. R.

Ultramicroscopic Investigation of Manganous Arsenate Jellies. FR. FLADE, H. SCHERFFIG, and E. DEISS (*Zeitsch. anorg. Chem.*, 1921, **116**, 228—230).—The observations of Deiss (A., 1914, ii, 371) on the formation and properties of manganous arsenate jellies and their gradual crystallisation have been confirmed. Glycerol retards the crystallisation to some extent. Reproductions of ultra-photomicrographs show the fibrous structure of the jellies and the change of structure which accompanies ageing.

E. H. R.

The Retarded Solution and Premature Precipitation of Iron Carbide in Steels and the Influence of the Initial State on these Phenomena. A. PORTEVIN and P. CHEVENARD (*Compt. rend.*, 1921, **172**, 1490—1493).—A study of a differential curve of dilatation of an eutectic steel shows a period of marked dilatation with heating consecutive to the transformation *Ac*. This anomaly has been interpreted as a manifestation of the retardation of solution of the cementite and shows a smaller amplitude as the temperature is increased less rapidly. Similarly, when the homogeneity of the solid solution is not realised, there is observed during cooling and a little before the commencement of the transformation *Ar* a region of marked dilatation. The steel appears to be hypereutectoid, or, in other words, there is premature precipitation of the cementite. This is confirmed by a comparison of the two curves for the same steel obtained in one case when the steel was coalesced, the metal having been previously annealed in such a way as to contain the

cementite in the globular state, whilst in the second case the steel was regenerated by several heatings followed by rapid cooling, resulting in a perlitic structure. The premature precipitation is manifest in the first case, but does not appear in the second.

W. G.

The Reaction between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron. IV. V. FALCKE (*Zeitsch. Elektrochem.*, 1921, **27**, 268—278. Compare A., 1913, ii, 327; 1915, ii, 169; 1916, ii, 484).—The author's own earlier work and that of Schenck and others (A., 1905, ii, 519; 1907, ii, 470) is reviewed and criticised. In a recent paper (A., 1918, ii, 355), Schenck throws doubt on the author's observation that ferrous oxide can be reduced by graphite at temperatures at which pure amorphous carbon is inactive. Fresh experiments have now shown that both ferrous and ferric oxide can be reduced completely by mixing with rather more than the theoretically necessary amount of graphite, compressing into tablets and heating at 900—1000° whilst the gases evolved are pumped away. The product obtained was not pure iron mixed with excess of graphite, as was previously obtained, but contained combined carbon.

To test further Schenck's theory that free carbon is an active constituent of the solid phase of the reaction between ferrous oxide and graphite and between carbon monoxide and iron, fresh determinations of the equilibrium constant were made for these two reactions and for the reaction $C+CO_2 \rightleftharpoons 2CO$ at temperatures between 600° and 750°, the equilibrium for the last reaction being measured in presence of metallic nickel. The values of the equilibrium constants did not correspond, and it is concluded that elementary carbon plays no part in the equilibrium of the two reactions above. The earlier conclusion that carbides are formed and determine the equilibrium explains best the experimental results.

E. H. R.

Microscopic Forms of Iron Rust. ADOLF ACKERMANN (*Kolloid Zeitsch.*, 1921, **28**, 270—281).—The rusting of small particles of iron, spongy iron, and iron wire in a moist atmosphere and in an atmosphere containing acid vapours, has been observed under a microscope. The forms assumed by the rust have been reproduced in drawings and photographs. It is shown that forms taken up by the rust depend in the first place on the formation of ferric hydroxide. This colloidal substance assumes forms and passes through formation processes which are very like the forms and processes which occur in organised nature. Non-rigid threads are formed which grow like organic fibres and which move and change their form when subjected to changes in the external conditions, for example, temperature. Under certain conditions, cell formation is exhibited, which externally, at least, is similar to organic cell formation. Drops of a solution of ferric hydroxide possess properties which are otherwise only found in organic cells. They exhibit a solid or semi-solid enclosing semi-permeable membrane or cell-wall, an adhering colloidal layer, and a nucleus.

Such drops grow, become broader, and divide in exactly the same manner as is observed in the division of organised cells. J. F. S.

Action of Sodium Carbonate on Solutions of Chrome Alum. L. MEUNIER and P. CASTE (*Compt. rend.*, 1921, **172**, 1488—1490).—The amount of sodium carbonate necessary to produce a permanent precipitate in a solution of chrome alum varies with the age and method of preparation of the solution. Immediately after the solution has been prepared, there is a relatively short period during which the amount of sodium carbonate required increases with the time up to a maximum which varies with the dilution and the temperature. This period is longer and more marked the more concentrated is the solution and the lower the temperature. After this maximum, there is a relatively long second period, which may last several months, during which the amount of sodium carbonate required decreases slowly with the time. At high temperatures, and particularly at 100°, the two periods are of such short duration that the end of their combined action is almost immediate.

Immediately on its dissolution in water, chromium sulphate undergoes a partial hydrolysis resulting in a provisional equilibrium. The chromium hydroxide and chromium sulphate interact to give a less ionised complex more stable towards sodium carbonate. This process predominates at first. This immediate hydrolysis progresses and is slowly accentuated (compare Tian, this vol., ii, 439, 440) and the ionic concentration is increased until the second process gradually predominates, with the consequent requirement of less sodium carbonate for the precipitation of the chromium hydroxide. W. G.

Tungsten–Nickel Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1921, **116**, 231—242).—Tungsten-nickel alloys containing from 0—80% of tungsten were prepared and examined thermally and microscopically. With the alloys richer in nickel, the accurate observation of the temperatures of the thermal effects, both of crystallisation and transition in the solid state, is rendered difficult owing to supercooling, which is liable to occur. Alloys containing more than 50% of tungsten lose their fluidity and become more pasty with increasing tungsten content at the highest temperature which could be employed for their preparation, 1600°. For alloys containing 0—35% of tungsten, the crystallising temperature rises from 1475° to 1525°, whilst a second, very irregular thermal effect is observed below 900°, becoming steady at 905° with 35% of tungsten. The maximum crystallisation point at 1525° corresponds with the composition Ni_6W. From 35% of tungsten the crystallisation curve falls to 1510° at 47% of tungsten, this being the limiting composition for complete miscibility. There is a eutectic point at 52% of tungsten, 1510°, the eutectic consisting of saturated mixed crystals of Ni_6W and tungsten with pure tungsten. The secondary thermal effect which, in alloys containing from 45% of tungsten upwards, is constant at 905°, appears to be due to the separation of saturated mixed crystals into their

constituents Ni_6W and tungsten. The limiting composition for ferromagnetism at the ordinary temperature in the alloys is between 10% and 20% of tungsten. The separation of the mixed crystals into their constituents at 905° is probably due to the transformation of the nickel from the β- to the α-form. E. H. R.

Titanium Hydride. ALBERT KLAUBER (*Zeitsch. anorg. Chem.*, 1921, **117**, 243—248).—The existence of a hydride of titanium has been proved by the method employed by Paneth and Nörring (A., 1920, ii, 758) for establishing the existence of a hydride of lead. When the gases from the titanium electrode were passed through a heated hard-glass tube (as in the Marsh test for arsenic), a deep black, highly metallic mirror appeared, shading off into greyish-black in the immediate vicinity of the flame, and on the other side through violet to reddish-brown. The best results were obtained with 0·1 to 0·2*N*-sulphuric acid as the electrolyte at 40—45°, using as cathode a hard-glass tube filled with gypsum and tipped with titanium. The identity of the titanium deposit in the heated tube was established by a number of microchemical tests. The gaseous hydride of titanium is odourless and tasteless. It is condensed at the temperature of liquid air, and can be revaporised by allowing the temperature to rise. Dilute solutions of sodium and potassium hydroxide, sodium carbonate, and silver nitrate absorb the gas. E. H. R.

The Crystalline Structure of Antimony and Bismuth. A. OGG (*Phil. Mag.*, 1921, [vi], **42**, 163—166).—The conclusion of James and Tunstall (A., 1920, ii, 548) is confirmed, that the unit rhomb contains eight atoms in the case of both antimony and bismuth. The edge of the unit antimony rhomb is 6·20 A.U., the structure consisting of two interpenetrating face-centred lattices. The shortest distance between the centres of two atoms is 2·92 Å.U. The length of the edge of the bismuth rhomb is 6·52 Å.U. The spacing of the planes differs somewhat from that of James and Tunstall. J. R. P.

The Crystalline Structure of Bismuth. R. W. JAMES (*Phil. Mag.*, 1921, [vi], **42**, 193—196).—The unit rhomb contains eight atoms. The length of the edge of the unit rhomb is 3·28 A.U. The distance of closest approach between two atomic centres is 3·11 Å.U. J. R. P.

The Action of Sodium Hyposulphite on Metallic Salts of the Platinum Group. GÉZA SAILER (*Zeitsch. anorg. Chem.*, 1921, **116**, 209—212).—When sodium platinichloride is reduced with sodium hyposulphite in excess, a dark, reddish-brown solution is obtained which, on slow evaporation, deposits a reddish-brown precipitate, consisting of a mixture of complex sodium platinosulphite compounds with $Na_2Pt_4S_6$. Later reddish-brown crystals of $Na_4[Pt''''(SO_3)_3(OH)_2]H_2O$ separate. When these are filtered off and the solution is further evaporated, bright yellow crystals of *sodium platinothiosulphate*, $Na_6[Pt''(S_2O_3)_4],10H_2O$, are obtained.

The complex sulphite compounds are precipitated from the reduced solution by alkalis, neutral salts such as potassium chloride, or by large excess of hyposulphite. When the reduction is carried out in acid solution, the acid decomposition products of the above reduction products are obtained. Alkaline reduction of palladium salts appeared to give only palladium sulphide. By neutral reduction of iridium chloride, $IrCl_4$, *sodium iridosulphite*, $Na_6[Ir''(SO_3)_4],10H_2O$, was obtained in bright yellow crystals. A new *rhodium* compound, $Na_6[Rh''_4(SO_3)_7],12H_2O$, was obtained as a brownish-red precipitate by reduction of sodium rhodium sesquichloride, $Na_6Rh_2Cl_{12}$, in neutral or alkaline solution. A greenish-yellow solution of sodium osmichloride, Na_2OsCl_6, becomes reddish-brown on addition of sodium hyposulphite, and after prolonged boiling a dull violet precipitate forms, which is a new compound, $Na_6[Os''_4(SO_3)_7],24H_2O$. Ruthenium sesquichloride, Ru_2Cl_6, reduced in the warm, also gave a new compound, $Na_3H_3[Ru''(SO_3)_4]$. E. H. R.

Hexachlororuthenates [Ruthenichlorides]. F. KRAUSS (*Zeitsch. anorg. Chem.*, 1921, **117**, 111—120).—In a previous paper it was shown (Gutbier and Krauss, A., 1915, i, 120) that ruthenichlorides of organic ammonium compounds could be prepared by leading chlorine into a concentrated hydrochloric acid solution of the corresponding ruthenochlorides, but alkali ruthenichlorides have not yet been obtained, even in presence of excess of chlorine. *Cæsium ruthenichloride* has now been prepared by dissolving ruthenium tetroxide in hydrochloric acid at the ordinary temperature under reduced pressure, to obtain a solution containing 1·7% of ruthenium, and adding a 5% solution of cæsium chloride. The solutions are thus chosen to be as concentrated as possible, so that the ruthenichloride separates at once. After washing with warm hydrochloric acid and drying, it has the composition $Cs_2[RuCl_6],H_2O$, and forms small, reddish-brown crystals, easily soluble in warm dilute hydrochloric acid with a bright red colour which quickly changes to a very dark red. The ruthenium is completely precipitated from solution by hydrogen sulphide; no other ruthenium compounds behave in this manner. Attempts to prepare the corresponding rubidium and potassium salts gave products more or less contaminated with ruthenochloride. E. H. R.

Reduction of Osmic Acid by Fats. J. R. PARTINGTON and D. B. HUNTINGFORD (*J. Roy. Micr. Soc.*, 1921, i, 15—19; from *Physiol. Abstr.*, 1921, **6**, 238).—The black substance formed by the reduction of osmic acid (osmium tetroxide, OsO_4) by olein in tissue staining is a hydrated form of osmium dioxide (OsO_2), probably $OsO_2,5H_2O$. E. S.

Mineralogical Chemistry.

Presence of Zinc in Malachite from Chessy. C. PERRIER (*Atti R. Accad. Lincei*, 1921, [v], **30**, i, 309—311).—It has been shown that rosasite, to which Lovisato attributed the formula $2CuO,3CuCO_3,5ZnCO_3$, is in reality a basic zinc–copper carbonate with the constitution $(Zn,Cu)CO_3,Cu(OH)_2$, which is analogous to that of malachite. Thus, rosasite resembles aurichalcite, in which also part of the zinc is replaced by copper. Analysis of a sample of pure, crystallised malachite from Chessy gives the results :

H_2O.	CO_2.	CuO.	ZnO.	Fe_2O_3.	PbO.	Residue.	Total.
8·36	19·87	71·31	0·45	0·04	trace	trace	100·03

In molecular proportions, these figures correspond with $1·02H_2O : 1·00CO_2 : 1·99(CuO+ZnO)$, so that the sample represents a typical malachite in which a small, but appreciable, proportion of the copper is replaced by zinc. T. H. P.

Analytical Chemistry.

Gas-absorption Flask. WALZ (*Chem. Zeit.*, 1921, **45**, 658).—A characteristic feature of a modified gas-absorption flask is a hollow stopper, prolonged as a closed tube with perforations in the end and extending to the base of the flask. The wide portion of the stopper fitting into the neck of the flask has a depression opposite the inlet tube, and an aperture opposite the outlet tube, of the flask. Gas drawn into the flask passes downwards through the absorbing substance into the base of the tubular part of the stopper and upwards to the aperture opposite the outlet. Apart from its simplicity and lightness, the apparatus offers the advantage of being readily emptied, and choking is prevented by rotating the stopper. W. J. W.

Poirrier's Blue C4B as an Indicator. W. MESTREZAT (*J. Pharm. Chim.*, 1921, **23**, 489—494).—Poirrier's Blue C4B cannot be recommended for use as an indicator in acidimetry; the colour change at the end-point is not sharp, and is still less so when carbonates are present. W. P. S.

Determination of Hydrogen-ion Concentration by means of Indicator Papers. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 961—970).—In determinations of the hydrogen-ion concentration in small quantities of solutions, indicator papers give results in close agreement with those obtained with indicator solutions, provided sufficient of a buffer mixture is used. The

papers should be prepared from hardened filter-paper. To ensure uniformity, the drop of the solution should be applied by means of a marked capillary, and the comparison of the colour with a standard should be made before the drop has dried. From an investigation of a number of indicator papers, the following values for p_H between which they are effective were obtained: congo-red, 2·5—4·0; methyl-orange, 2·6—4·0; blue lacmoid, 4·8—6·0; alizarin, 4·6—5·8; metachrome-red, 6·0—8·5; brilliant yellow 6·8—8·0; red litmus, 6·6—8·0; blue litmus, 6·0—7·8; azolitmin, 6·0—8·0; α-naphtholphthalein, 8·2—9·5; and curcumin, 7·5—9·5. Hæmatoxylin paper may be used for strong acids; methyl-red, phenolsulphonphthalein, rosolic acid, and neutral red have not proved suitable for determining p_H. W. J. W.

Iodometric Estimations by Stortenbeker's Method. D. DE MIRANDA and A. E. ROEST VAN LIMBURG (*Chem. Weekblad*, 1921, **18**, 419—420).—To determine the point at which chlorine ceases to be evolved in iodometric estimations by Stortenbeker's method (A., 1890, 1185), a side branch with a tap is fused into the delivery tube of the retort, and connected by means of a ground glass joint with a vessel containing iodide–starch solution. The gas is periodically tested with this solution, and the latter eventually returned to the retort, thus avoiding loss. W. J. W.

Estimation of Soil Acidity by means of the Iodine Method. O. LEMMERMANN and L. FRESENIUS (*J. Landw.*, 1921, **69**, 97—104).—The method based on the liberation of iodine from potassium iodide–iodate mixture by the soil acids (A., 1915, ii, 655) has several weak points. Iodine is adsorbed by the soil, thus lowering the apparent acidity figure; iodine may be liberated from the reagent by organic matter; and the time of contact of soil and reagent largely influences the result obtained. Iodine adsorption may be corrected for by a previous determination of the adsorption curve, and subsequent calculation for the particular conditions of the experiment. The liberation of iodine is incomplete after the fifteen minutes' contact suggested by Stutzer and Haupt, and better results are obtained with a contact period of two hours. The method is considered too complicated and uncertain to be of any great value. A. G. P.

Titration of Bases Combined with Weak Acids, and of Very Weak Bases with Acids, and Vice Versâ. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 885—896).—With tropæolin-OO or -O as indicator, acids and bases having a dissociation constant above 10^{-10} may be titrated with an accuracy of 1%. Acids may also be titrated when combined with bases, or vice versâ, with a dissociation constant equal to or less than 10^{-4}. W. J. W.

Detection and Estimation of Minute Quantities of Bromide in Saline Residues, and in a Mixture of the Halogens. A. J. JONES (*Pharm. J.*, 1921, **106**, 475—477).—To detect the presence of a bromide in a chloride or in a saline residue (this must be free from ammonium salts and organic matter), 5 c.c. of a 10% solution

of the sample are placed in a small distillation flask, 1 drop of dilute thymol-blue solution is added, followed by *N*/1-sulphuric acid in quantity just sufficient to give a rose-pink coloration; after the addition of 0·3 c.c. of permanganate solution (potassium permanganate 5 grams, phosphoric acid, *d* 1·75, 6·25 c.c., and water to 100 c.c.), the mixture is heated at 85° and a current of air is passed through it. The air and vapours are then conducted through a U-tube containing 5 c.c. of magenta reagent. With a quantity of bromine equivalent to 1·0 c.c. of *N*/1000-potassium bromide solution a distinct purple coloration develops in the U-tube. The coloration becomes more distinct when the contents of the U-tube are shaken with 7 c.c. of chloroform. The test may be rendered quantitative by comparing the coloration with those given by known amounts of bromine. If iodides are present, the iodine must be removed previously by treating the solution with sodium nitrite and phosphoric acid and shaking it with chloroform. The magenta reagent is prepared by adding 100 c.c. of a 0·1% magenta solution to a cold mixture of 60 c.c. of water and 40 c.c. of sulphuric acid; after twenty hours, the yellow solution is ready for use when mixed with its own volume of glacial acetic acid. W. P. S.

Argentometric Titration of Iodides. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 917—920).—In estimating iodides by titration with silver nitrate, a difficulty in determining the end-point is overcome by adding a colloid to hold the precipitated silver iodide in suspension. Starch solution used as indicator, if in sufficient amount, achieves this object. When 25 c.c. of *N*/10-iodide solution, 10 c.c. of 0·00008—0·0001*N*-iodine solution, and 20 c.c. of 2% starch solution are titrated with *N*/10-silver nitrate, the blue colour changes first to green and then to light green, and by adding excess of the reagent a colour change to yellow occurs which is readily detected. Bromide and chloride, not exceeding 3% and 20% respectively, do not influence the reaction. Either acid or neutral solutions may be used, and accurate results may be obtained even with low concentrations. No advantage is gained by using palladium salts as indicators as recommended by Schneider (A., 1918, ii, 205). W. J. W.

Estimation of Dissolved Oxygen in Water. REINALDO VANOSSI (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 96—120).—A review of methods employed for the estimation of dissolved oxygen in water. The Winkler iodometric method is discussed in detail.
G. W. R.

Estimation of Sulphur in Oils. ENRIQUE HAUSER (*Anal. Fís. Quím.*, 1921, **19**, 175—191).—In the method described, the substance under examination is burnt in a closed vessel filled with oxygen, ignition being effected by means of an electric coil. After cooling and introduction of a dilute solution of sodium peroxide to oxidise sulphurous acid, the vessel is washed out and, after addition of a little bromine water to ensure complete oxidation, sulphur is estimated as sulphate in the united washings. The

method is considered generally applicable to the determination of sulphur in organic compounds. [See, further, *J. Soc. Chem. Ind.*, 1921, Aug.] G. W. R.

Estimation of Nitrogen in Nitrates by Arnd's Method. O. NOLTE (*Zeitsch. anal. Chem.*, 1921, **60**, 167—168).—The method described by Arnd (A., 1917, ii, 504) is trustworthy. W. P. S.

Estimation of Nitrates in Bismuth Salts by means of Titanium Chloride and Devarda's Alloy. THOS. MCLACHLAN (*Pharm. J.*, 1921, **106**, 477—478).—Reduction of the nitrate by titanium trichloride is best effected in approximately neutral solution, a slight excess of alkali being added subsequently, but previously to the distillation of the ammonia. A more convenient and trustworthy method for the estimation of nitrate in bismuth carbonate or other salt consists in mixing 5 grams of the sample with 150 c.c. of water, 5 c.c. of alcohol, and 50 c.c. of 33% potassium hydroxide solution, and adding 8 grams of Devarda's alloy; after ten minutes, the ammonia is distilled and titrated in the usual way. W. P. S.

The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. VI. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1921, **117**, 91—102. Compare A., 1919, ii, 426).—A critical review of previous work on the estimation of phosphoric acid or magnesium by precipitation as magnesium ammonium phosphate. Neubauer's method, or a single precipitation on the cold, is not to be recommended, as it gives accurate results only under special conditions. The double precipitation method gives good results only if the first precipitate is dissolved in not too little hydrochloric acid, if only Cl' and NO'_3 anions and no large quantity of alkali kations are present during precipitation, and the second precipitation is carried out by quick addition of 10% ammonia solution. Jörgensen's method (A., 1906, ii, 579; 1911, ii, 536) is inaccurate and Järviner's method (A., 1905, ii, 62, 555) gives low results. The only method which, under the right conditions, gives a pure product and an accurate result is that of Schmitz (A., 1919, ii, 426). This method is accurate under widely varying conditions, since the errors cancel one another. E. H. R.

Estimation of Small Quantities of Phosphate in Glycerophosphates. J. L. LIZIUS (*Pharm. J.*, 1921, **106**, 478—479).—One gram of the glycerophosphate is dissolved in dilute nitric acid, the solution is diluted to 50 c.c., and 10 c.c. of this solution are added to a mixture of 10 c.c. of 25% nitric acid and 10 c.c. of 10% ammonium molybdate solution; the yellow coloration obtained is compared with that produced by 5 c.c. of 0·004% phosphoric acid solution under the same conditions. If the colorations are of equal intensity, the sample contains 0·1% of inorganic phosphoric acid; should the colorations be different, the quantities of test solution or standard phosphoric acid solution used are varied accordingly. In the case of ferric glycerophosphate, the sample is dissolved in warm dilute nitric acid, sodium hydroxide is added,

the ferric hydroxide separated by filtration, and the filtrate diluted to 50 c.c. and used for the estimation. W. P. S.

Arsenic as a Normal Constituent of Soils. FEDERIGO REICHERT and ROGELIO A. TRELLES (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 89—95).—In the estimation of arsenic in soils, the air-dried soil is heated with a mixture of sulphuric and nitric acids (1 : 2) on a sand-bath until nitric acid is eliminated. The residue is extracted with water. Arsenic is estimated in an aliquot portion of the filtrate after precipitation together with the hydroxides of iron and aluminium by means of aqueous ammonia. Examination of soils from various parts of the Argentine shows that arsenic is a constant constituent, but that it is not possible to correlate its amount with the chemical composition of the soil. Up to 2·25 mg. per 100 grams of soil were found. The amount of arsenic found is greater at the surface than in the lower strata of the soil (compare Zuccari, A., 1913, ii, 151—152; 1914, i, 128). G. W. R.

Volumetric Estimation of Arsenic Acid and Arsenates. R. LEITCH MORRIS (*Pharm. J.*, 1921, **106**, 486—488).—The method described in the British Pharmacopœia is untrustworthy owing to the fact that the mixing of the reagents alone causes a liberation of iodine; the solution must not be diluted before titration, or reversal of the reaction occurs, and a further error, but in the opposite direction, is due to the action of the relatively concentrated acid on the thiosulphate. If, however, the titration is commenced as soon as the arsenate solution has been mixed with the hydrochloric acid and iodide solution, the thiosulphate solution being introduced drop by drop with constant stirring, and the titration finished in five minutes, the error is fairly constant and may be corrected by deducting 0·0040 gram from the actual quantity of disodium hydrogen arsenate found by the titration. The presence of nitrates in any considerable quantity interferes with the estimation. W. P. S.

Estimation of Sodium Arsenate. C. E. CORFIELD and ELSIE WOODWARD (*Pharm. J.*, 1921, **106**, 473—475).—Comparison of various methods showed that the one described by Gooch and Morris (A., 1900, ii, 686) is trustworthy; this also applies to Williamson's method, provided that the calculation is made from the iodine titration. The method described in the British Pharmacopœia does not make allowance for the inaccuracy of the thiosulphate titration and, consequently, the error amounts to about 1%. W. P. S.

The Estimation of Total Carbon and a New Method of Estimating Graphitic Carbon in Ferrous Alloys. P. WENGER and A. TRAMPLER (*Helv. Chim. Acta*, 1921, **4**, 547—551).—Comparative examination of the methods of Corleis's, and of the electric, furnace method with iron containing 0·2—8·3% of impurities has led the authors to the conclusion that the results obtained by the latter method are more concordant among themselves than those given by Corleis's process, that the furnace method is much more rapid,

and is universally applicable, and, lastly, that it does not involve a preliminary treatment with chlorine, which invariably induces a small error in the estimation of carbon.

The use of phosphoric acid in the estimation of graphitic carbon has also been investigated. The method consists in heating the phosphoric acid (*d* 1·7) in a platinum capsule to at least 150° and gradually introducing the finely-divided alloy, 100 c.c. of acid being used for each gram of the latter. A small residue generally remains unattacked, and the original acid is therefore decanted and replaced by 25 c.c. of fresh acid. The mixture is filtered without dilution through a Gooch crucible, the residue washed with water (300 c.c.) and the carbon ultimately burnt in the electric furnace. The method is applicable to ferromanganese, ferrovanadium, ferrochrome, and ferrosilicon. Certain alloys are, however, incompletely attacked, but the addition of sulphuric, hydrochloric, or nitric acid to the phosphoric acid is of no advantage. The presence of hydrofluoric acid enables the method to be applied satisfactorily to ferrosilicons containing not more than 60—65% of silicon. The addition of metallic catalysts, such as platinum or mercury, does not yield satisfactory results. H. W.

A New Method for Determining the Volatile Matter yielded by Coals up to Various Temperatures. WILLIAM ARTHUR BONE and LEONARD SILVER (T., 1921, **119**, 1145—1152).

Volumetric Estimation of Potassium. ST. MINOVICI and C. KOLLO (*Bul. Soc. Chim. România*, 1921, **3**, 17—25).—About 0·25 gram of the potassium salt is dissolved in 5 c.c. of water, 0·5 gram of sodium hydrogen tartrate is added, and the mixture is stirred occasionally during one hour. Five c.c. of 5% tartaric acid solution saturated with potassium hydrogen tartrate are then added; the precipitated potassium hydrogen tartrate is collected on a filter, washed with the tartaric acid solution (about 20 c.c.), then with 40 c.c. of alcohol, and, finally, with 50 c.c. of a mixture of equal volumes of alcohol and ether. The precipitate may be dried and weighed, or it may be dissolved and titrated in the usual way. W. P. S.

Detection and Estimation of Potassium as Picrate. ST. MINOVICI and AL. IONESCU (*Bul. Soc. Chim. România*, 1921, **3**, 25—33).—The reagent used is a saturated solution of picric acid in 95% alcohol containing 5% of glycerol. A drop of this reagent yields characteristic crystals of potassium picrate when added to a drop of a solution containing a potassium salt. Ammonium and sodium salts do not yield crystals, but small crystals may, however, appear at the edge of the drop where more rapid evaporation occurs. When applied as a microchemical test, the limit of sensitiveness is about 0·01 mg. of potassium. To estimate potassium, the potassium picrate precipitate may be collected, washed with ether, dried under reduced pressure, and weighed, or the precipitate may be dissolved and titrated with quinine hydrogen sulphate solution; in very dilute sulphuric acid solution quinine sulphate precipitates picric acid completely. W. P. S.

Use of Hypophosphorous Acid in Gravimetric Analysis. Estimation of Silver and its Separation from Lead and other Metals. L. MOSER and TH. KITTL (*Zeitsch. anal. Chem.*, 1921, **60**, 145—161).—The boiling solution of silver nitrate is treated with an excess of hypophosphorous acid and, when the black precipitate of silver has coagulated it is collected, washed with hot water, dried, and weighed. The authors find that the use of hot water for washing the precipitate does not cause the latter to pass through the filter as stated by Mawrow and Mollow (A., 1909, ii, 183). The silver nitrate solution must be neutral and the concentration not more than $N/20$, otherwise hypophosphorous acid is occluded by the precipitate. The separation of silver from lead, zinc, cadmium, etc., depends on the solubility of the hypophosphites of these metals in hot water. W. P. S.

Separation and Estimation of the Alkaline-earth Metals. (MLLE) VIRGINIE TEODOSSIU (*Bul. Soc. Chim. România*, 1921, **3**, 34—40; compare this vol., i, 540).—A solution containing calcium, strontium, and barium salts is heated with sulphuric acid, cooled, mixed with twice its volume of alcohol, and, after four hours, the supernatant liquid is decanted through a filter. The precipitate containing the mixed sulphates is then treated with a few drops of ammonia to neutralise the remaining sulphuric acid and ammonium citrate solution is added; the latter dissolves the calcium sulphate and, after three hours, the solution is separated by filtration from the insoluble strontium and barium sulphates and the calcium estimated in the filtrate. The barium and strontium sulphates are then ignited, boiled with ammonium carbonate solution, the strontium carbonate is dissolved by the addition of hydrochloric acid, and the solution separated from the insoluble barium sulphate. The ammonium citrate solution is prepared by dissolving 42 grams of citric acid in water, neutralising the solution with ammonia, and diluting it to 1 litre. W. P. S.

Gravimetric Analysis. XVII. Estimation of Zinc. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1921, **34**, 235—236).—In the absence of potassium salts, zinc may be estimated by precipitating it as ammonium zinc phosphate. The zinc solution, measuring 100 c.c. and containing about 0·1 gram of zinc, is treated with 2 grams of ammonium chloride, boiled, and 10 c.c. of 20% diammonium hydrogen phosphate solution are added. After eighteen hours, the precipitate is collected, washed with 50 c.c. of water saturated previously with ammonium zinc phosphate, dried at 130°, and weighed, or the precipitate may be ignited and weighed as zinc pyrophosphate. For a weight of about 0·3 gram of precipitate, a correction of +0·3 mg. is made for the dried precipitate, and of +0·9 mg. in the case of the ignited precipitate. W. P. S.

Estimation of Mercury in its Ores. A. HEINZELMANN (*Chem. Zeit.*, 1921 **45**, 657—658).—The finely-pulverised ore is placed in a thin-walled tube, 170 mm. × 17 mm. diam., and mixed with an equal amount of lime; a layer of lime and a small quantity of

long-fibre asbestos are placed above the mixture. In presence of much sulphur, iron filings must be added. The tube is loosely clamped in an almost horizontal position, and the mixture is heated for two to three minutes over a small flame, and then strongly for ten minutes, the tube being rotated at intervals. The portion of the tube containing the sublimed mercury is cut off, the mercury is dissolved in nitric acid (*d* 1·48—1·50), a few drops of *N*/10-potassium permanganate are added, and the solution is titrated with *N*/20-potassium thiocyanate solution. W. J. W.

Volumetric Estimation of Aluminium in its Salts. ALFRED TINGLE (*J. Ind. Eng. Chem.*, 1921, **13**, 420—422).—Comparison of methods for the estimation of aluminium by titrating its salt in solution with sodium hydroxide solution, using phenolphthalein as indicator, showed that two only are trustworthy. In the first, the aluminium sulphate solution is boiled and titrated with *N*/2-sodium hydroxide solution until the pink colour of the indicator persists after boiling for one minute. The second method is similar except that the aluminium sulphate solution is treated with an excess of barium chloride before being titrated; this method has some slight advantage over the first, particularly if iron salts are present, as the colour of the iron is masked by the barium sulphate. W. P. S.

Oxidimetric Estimation of Manganese in Hydrofluoric Acid Solution. JOSEF HOLLUTA and JOSEF OBRIST (*Monatsh.*, 1921, **41**, 555—571).—Manganese can be estimated in accordance with the equation: $MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} = 5Mn^{\cdot\cdot\cdot} + 4H_2O$ under the following conditions. The neutral or faintly acid solution of the manganous salt, which must not contain more than 0·2 gram Mn, is placed in a 850—1000 c.c. Erlenmeyer flask and diluted to 300 c.c.; after addition of sulphuric acid (1 : 7, 5—10 c.c.) and ammonium fluoride (5 grams), the cold solution is titrated with *N*/10-permanganate. The greater part of the latter is immediately decolorised, but sooner or later, in accordance with the amount of manganese present, the liquid becomes reddish-yellow. The end-point is fixed by observation of the absorption spectrum of the solution with a pocket spectroscope, a matt 50 c.p. metallic filament lamp being used as source of illumination. The titration is considered to be finished when the bands at 547·3 and 525·6$\mu\mu$ persist for more than five minutes. An excess of fluorine ions, low hydrogen-ion concentration, low temperature, and considerable dilution are essential. The presence of ferric iron in large amount, of chlorine, and of nitrate ions causes no disturbance. If the titre of the permanganate is estimated by the fluoride method, the results are as accurate as those of the best volumetric methods described hitherto. H. W.

Approximate Estimation of Iron and Manganese in Systematic Qualitative Analysis. L. J. CURTMAN and N. H. HECHT (*Chem. News*, 1921, **122**, 254—255).—A hydrochloric acid solution containing iron, aluminium, chromium, manganese, and zinc is boiled with the addition of sodium hydroxide and sodium peroxide, the precipitated ferric hydroxide, etc., is collected, dissolved in

dilute hydrochloric acid, potassium thiocyanate is added, and the mixture titrated with standardised stannous chloride solution. To estimate the manganese, another portion of the original hydrochloric acid solution is treated as described with sodium hydroxide and peroxide, the precipitate collected, washed until free from chlorides, dissolved in nitric acid, the manganese oxidised by sodium bismuthate under the usual conditions, and the resulting permanganate titrated with standardised hydrogen peroxide solution.

W. P. S.

Reductions with Zinc and Cadmium in Volumetric Analysis. W. D. TREADWELL (*Helv. Chim. Acta*, 1921, **4**, 551—565).—The rapid reduction of solutions of ferric salts by finely-divided zinc only occurs in solutions which are but slightly acid, and the danger is then present that a portion of the iron may be deposited on the zinc; in addition, it is difficult to devise a satisfactory correction for the iron present as impurity in the zinc. These disadvantages can be circumvented by substituting cadmium for zinc, the metal being obtained in a sufficiently finely-divided and non-spongy condition by the electrolysis of concentrated cadmium sulphate solution acidified with sulphuric acid between platinum electrodes; the size of the particles can readily be controlled by altering the current density. Reduction of the ferric sulphate solution occurs very rapidly and without noticeable evolution of hydrogen. The degree of acidity of the solution has no effect on the reaction. The method is well adapted to the estimation of very small quantities of iron.

[With A. RHEINER.]—Quadrivalent titanium is also quantitatively reduced by finely-divided cadmium. Titanium and iron may be estimated simultaneously by complete reduction, followed by titration with standard potassium permanganate; the end-points are conveniently determined electrometrically, or, if this method is not available, by use of potassium thiocyanate as outside indicator. In like manner, molybdenum trioxide is quantitatively reduced to the sesquioxide. Ammonium vanadate is uniformly reduced to the stage $V_2O_{2\cdot046}$; possibly the slight divergence from the bivalent stage is due to reoxidation. The experiments are best performed by running the reduced solution directly into an excess of standard permanganate and titrating the latter with oxalic acid. Uranyl sulphate is likewise smoothly reduced, and the concordance of the results makes it probable that the action proceeds exactly to the uranous stage, but this matter is one for further examination.

H. W.

A Micro-method for the Estimation of Iron in Organic Combination. MAURICE NICLOUX and GEORGES WELTER (*Bull. Soc. Chim. Biol.*, 1921, **3**, 170—173).—The method depends on the conversion of the iron into ferric oxide by ignition of the organic compound, and the subsequent reduction of the oxide to metallic iron by heating in a current of hydrogen; the loss of weight on reduction is taken as a measure of the iron present. The method is only applicable to pure compounds.

C. R. H.

Use of Cupferron [Ammonium Salt of Nitrosophenylhydroxylamine] in the Separation of Zirconium from Uranium. A. ANGELETTI (*Gazzetta*, 1921, **51**, i, 285—288).—In estimating zirconium and uranium present together, the former may be precipitated by means of cupferron in an acid medium, the uranium being subsequently precipitated by excess of ammonia solution as ammonium uranate, which is calcined in a current of hydrogen and weighed as UO_2; the small proportion of cupferron left in the filtrate does not interfere with the precipitation of the uranium. T. H. P.

Quantitative Separation of Arsenic, Antimony, and Tin. FRIEDRICH L. HAHN and PETER PHILIPPI (*Zeitsch. anorg. Chem.*, 1921, **116**, 201—205).—The method devised by Hahn (A., 1916, ii, 266) for the detection and qualitative separation of these elements can be used for their estimation. The precipitated sodium pyroantimonate adheres obstinately to the sides of the vessel and cannot therefore be weighed directly. The method adopted is as follows. After the sulphide solution has been completely oxidised with hydrogen peroxide, 80% alcohol equal to one-third of the volume of the solution is added, and after twenty-four hours the solution is filtered. The precipitate is washed with alcohol of increasing strength containing a little sodium carbonate, then dissolved in dilute hydrochloric acid containing tartaric acid, and transferred to the vessel in which it was precipitated, to dissolve the portion adhering to the vessel. The antimony can then be estimated by precipitation as sulphide. From the filtrate after evaporation of the alcohol, the tin is precipitated by addition of ammonium nitrate and weighed as SnO_2, and the arsenic finally determined by precipitation as magnesium ammonium arsenate. [Compare *J. Soc. Chem. Ind.*, 1921, Aug.] E. H. R.

Estimation of Glycerol in Wine by Conversion into Acraldehyde by means of Boric Acid. A. HEIDUSCHKA and F. ENGLERT (*Zeitsch. anal. Chem.*, 1921, **60**, 161—166).—The extract from 100 c.c. of wine is transferred to a small retort with 15 c.c. of water, evaporated to a volume of about 2 c.c., 1 gram of boric acid is added, and the heating continued until all water has been expelled. The retort is then connected with receivers containing ammonia and cooled in an ice and salt mixture, and the temperature is raised to 320°, a current of air being passed into the tubulus of the retort. After forty-five minutes, the receivers are disconnected, their contents mixed, 5 c.c. of *N*/10-silver nitrate solution are added, the mixture heated for about twenty minutes, and filtered. The excess of silver nitrate is titrated in the filtrate. The amount of glycerol corresponding with the volume of silver nitrate solution reduced is found by reference to a table. W. P. S.

Quantitative Test of the Thermal Stability of Glyceryl Nitrate Explosives. M. TALIANI (*Gazzetta*, 1921, **51**, i, 184—193).—The author describes an apparatus and method for following the gradual increase of the pressure developed when an explosive is maintained in a closed space at a constant temperature; glyceryl

nitrate and explosives derived from it are kept at 120° and cellulose nitrates at 135°. For a number of explosives the pressure–time curves have been traced, the results showing that these curves serve to characterise the different explosives with nitric esters as bases. [Compare *J. Soc. Chem. Ind.*, 1921, Aug.] T. H. P.

Generalisation of Salkowski's, Liebermann's, and Schiff's Reactions [for Cholesterol]. GALAVIELLE, PORTES, and CRISTOL (*Bull. soc. sci. médit. biol. Montpelier*, 1921, **2**, 129—132; from *Physiol. Abstr.*, 1921, **6**, 238—239).—In their work on the elimination of terpenes, the authors found that the above reactions for cholesterol sometimes give the same colour with these substances, but in other cases they are different. Schiff's reaction (solution in nitric acid, careful evaporation, and addition of ammonia) gives a yellow coloration with the acid and red with ammonia. This occurs with cholesterol and all terpenes examined, except menthol; in that case ammonia only deepens the yellow. The material, when simply touched with sulphuric acid, gives red with cholesterol, terpene, Borneo, sassafras, and buchu camphors, and terebenthene; yellow with Japanese camphor and synthetic camphor; brown with menthol. Salkowski's reaction (addition of sulphuric acid with agitation to a solution in chloroform) gives a red in the chloroform and green fluorescence in the acid with cholesterol; with terpene, the chloroform is not coloured and the acid is orange-red; with Japanese and synthetic camphor, the chloroform shows a yellow fluorescence and the acid is golden-yellow; with Borneo camphor and terebenthene, the chloroform is yellow and the acid orange-red; with sassafras-camphor, the chloroform is faint yellow and the acid cherry-red; with buchu-camphor the same occurs, except that the chloroform is only fluorescent; with menthol, the chloroform becomes cloudy and the acid orange. In Liebermann's reaction (addition of acetic anhydride and sulphuric acid to the solution in chloroform) cholesterol gives blue; terpene an evanescent yellow; Japan and synthetic camphor nil; Borneo camphor, buchu-camphor, and terebenthene reddish-brown; sassafras-camphor gold; and menthol cherry-red. E. S.

An Improved Form of Barfoed's Reagent. H. E. ROAF (*Proc. Physiol. Soc.*, 1920, *J. Physiol.*, 1921, **54**, lx—lxi; from *Physiol. Abstr.*, 1921, **6**, 170).—The most satisfactory reagent was found to be: copper acetate, 50 grams; sodium acetate, 50 grams; glacial acetic acid, 5 c.c.; water to 1000 c.c. With this reagent a reduction is obtained with 0·1% dextrose solution on merely heating to the boiling point, whilst 1% solutions of pure specimens of maltose or lactose do not show reduction under similar conditions. E. S.

Estimation of Dextrose in Glucosides. AL. IONESCU (*Bull. Soc. Chim. România*, 1921, **3**, 6—9).—A volumetric method, using ferricyanide, described recently by the author (this vol., ii, 220) may be applied to the estimation of dextrose resulting from the hydrolysis of certain glucosides. In the case of amygdalin, the hydrocyanic acid and benzaldehyde formed during the hydrolysis

must be expelled by heating the solution before the sugar is estimated. W. P. S.

A New Reagent for the Estimation of Sugar in Urine. J. B. SUMNER (*Proc. Amer. Soc. Biol. Chem.*, *J. Biol. Chem.*, 1921, **46**, xxi; from *Physiol. Abstr.*, 1921, **6**, 170).—4 : 6-Dinitroguaiacol is reduced to the intensely-coloured 4-nitro-6-aminoguaiacol when heated with solutions of dextrose in the presence of sodium carbonate. The reaction is quantitative, and lends itself to the colorimetric estimation of dextrose. The new reagent is not reduced by other urinary constituents. E. S.

Estimation of Dextrose, Lævulose, Sucrose, and Dextrin in the Presence of Each Other. A. BEHRE (*Zeitsch. Nahr.-Genussm.*, 1921, **41**, 226—230).—The dextrose is estimated iodometrically by the method described by Willstätter and Schudel (A., 1918, ii, 337); if the estimation is repeated after a portion of the sample has been heated with hydrochloric acid to invert the sucrose, the difference between the two estimations gives the amount of dextrose formed from the sucrose, and the quantity of the latter may be calculated. The method may also be used for the estimation of dextrose and dextrin in commercial "starch syrup," the additional quantity of dextrose found after the sample has been heated with hydrochloric acid for three hours being a measure of the dextrin. The authors have not yet determined the effect on the results due to the maltose which is present in "starch syrup." Lævulose may be estimated in a mixture of sugars by determining the cupric-reducing power after the dextrose has been oxidised by iodine in alkaline solution and the resulting gluconic acid removed by treatment with lead acetate. W. P. S.

The Official Method for the Estimation of Hydrocyanic Acid. C. E. CORFIELD and C. J. EASTLAND (*Pharm. J.*, 1921, **106**, 482—483).—Excess of ammonia interferes with the estimation of hydrocyanic acid by the method described in the British Pharmacopœia, the error increasing with increased concentration of the ammonia. Increase in the amount of potassium iodide used has no effect until the quantity added exceeds 10 c.c. W. P. S.

Estimation of Lecithin. J. L. B. VAN DER MARCK (*Pharm., Weekblad*, 1921, **58**, 989—992).—The estimation of phosphate in lecithin by the molybdate method is tedious and apt to give erroneous results. The author recommends precipitation as magnesium ammonium phosphate, after the customary removal of organic matter by means of nitric and sulphuric acids. Some doubt exists as to the correctness of the formula $C_{42}H_{84}O_9NP$ for lecithin and the purity of samples cannot therefore be determined from the ratio : $P_2O_5=2C_{42}H_{84}O_9NP$. W. J. W.

Estimation of Formaldehyde. C. KOLLO and O. LASCAR (*Bul. Soc. Chim. România*, 1921, **3**, 3—6).—A modification of Legler's method is described in which the hexamethylenetetramine formed is precipitated by the addition of an excess of picric acid, the precipitate removed by filtration, and the excess of picric acid

then titrated. Ten c.c. of a solution containing about 1 gram of formaldehyde are treated with 5 c.c. of ammonia, (*d* 0·960), and, after thirty minutes, the mixture is heated at 60° until the excess of ammonia has been expelled. The mixture is then cooled, treated with 50 c.c. of *N*/20-picric acid solution, diluted to 100 c.c., filtered after thirty minutes, and 50 c.c. of the filtrate are titrated with *N*/10-sodium hydroxide solution, methyl-red being used as indicator. Each c.c. of *N*/20-picric acid solution is equivalent to 0·009 gram of formaldehyde. W. P. S.

Titration of certain Alkaloids. NORMAN EVERS (*Pharm. J.*, 1921, **106**, 470—472).—Bromophenol-blue is the most suitable indicator for use in the titration of morphine, atropine, and normal quinine salts, and methyl-red in the titration of quinine hydrogen salts. W. P. S.

Analysis of Theobromine Sodium Salicylate. C. T. BENNETT and F. B. WINDLE (*Pharm. J.*, 1921, **106**, 472).—The following modification of the British Pharmacopœia method is recommended: Two grams of the dried salt are dissolved in 10 c.c. of water and the solution is titrated with *N*/1-hydrochloric acid, using phenolphthalein as indicator; not more than 5·5 c.c. of the acid should be required. The solution should now be slightly alkaline in reaction towards litmus; if not, a drop of dilute ammonia is added. After three hours, the precipitated theobromine is collected, washed with four quantities of 5 c.c. each of cold water, dried at 100°, and weighed; 0·13 gram is added to the weight found. The filtrate from the theobromine precipitate is treated with 5.5 c.c. of *N*/1-hydrochloric acid and extracted with four quantities of 10 c.c. of ether. The ethereal solution is washed with 10 c.c. of cold water, 50 c.c. of water are then added, and the salicylic acid is titrated with *N*/1-sodium hydroxide solution, using phenolphthalein as indicator. W. P. S.

Potassium–Zinc Ferrocyanide as a Precipitant for Urines. Its Application to the Separation and Estimation of Uric Acid and Xanthine Bases. THIÉRY (*J. Pharm. Chim.*, 1921, **23**, 494—503).—Two hundred c.c. of the urine are treated with 25 c.c. of a mixture of equal volumes of *N*/10-silver nitrate solution and a solution containing 150 grams of ammonium chloride and 100 grams of magnesium chloride per litre of ammonia, *d* 0·922; the treated urine is then filtered, and to 100 c.c. of the filtrate are added 10 c.c. of alkaline *N*/10-potassium cyanide solution and 20 drops of 10% potassium iodide solution containing 2% of ammonia, and the solution is titrated with *N*/10-silver nitrate solution until a persistent turbidity is obtained. The number of c.c. of *N*/10-silver nitrate solution used for the titration is multiplied by 0·21 to obtain the sum of the uric acid and xanthine bases (in terms of uric acid) expressed as grams per litre of urine. Another portion of 200 c.c. of the urine is treated with 20 c.c. of 15% potassium ferrocyanide solution and 20 c.c. of 11·2% zinc acetate solution; this precipitates the xanthine bases, and, after the mixture has been filtered, the uric acid alone is estimated in 110 c.c. of the

filtrate as described above. The difference between the two estimations gives the xanthine bases in terms of uric acid.

W. P. S.

Detection of Fluorescein in Very Dilute Solutions. MAURICE LOMBARD (*Bull. Soc. chim.*, 1921, [iv], **29**, 462—464).—To 30 c.c. of the solution a few drops of dilute sulphuric or hydrochloric acid, free from chlorine, are added, and then the solution is shaken with a small amount of ether. When the ether has separated, the ethereal layer being about 3 mm. thick, a few drops of aqueous ammonia are added and the tube is gently shaken round. The ethereal layer becomes green if fluorescein is present in the original solution, and the green colour passes gradually into the aqueous layer underneath. By this method it is possible to detect fluorescein at a dilution of 1 in 200,000,000. By using 200 c.c. of solution and slightly modifying the process by making a double ethereal extraction, it is possible to make the test sensitive at a dilution of 1 in 500,000,000. If an emulsion forms, tending to prevent the separation of the ethereal layer, one drop of alcohol is added.

W. G.

Characterisation of Amylase Solutions. H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. chem.*, 1921, **112**, 193—230).—The authors introduce a new and more absolute measure *Sf* for the activity of amylase preparations, analogous to that (*If*) previously recommended by them for invertase preparations (*Zeitsch. physiol. Chem.*, 1919, **106**, 201).

$Sf = K \times$ maltose (in grams)/enzyme preparation (in grams) where K is the constant of the unimolecular reaction according to which the first major portion of the hydrolysis proceeds and the maximum amount of maltose which can be formed. By calculation it is found: 1000 Lintner units=26 *Sf*; 1000 units of the "new scale" of Sherman and collaborators (A., 1910, ii, 1012; 1915, i, 183)=38·5 *Sf*. It is suggested that the reaction constant should be measured at 37° with soluble, previously boiled starch, prepared according to Lintner, in a concentration of 0·72—2·8% and with enzyme concentrations which under these conditions give a constant between 0·004 and 0·08. The optimum P_H should be secured, which the authors find to be =5. The paper contains a review of the earlier literature.

G. B.

Exact Demonstration of Tyrosinase. The Tyrosinase Reaction. HUGO HAEHN (*Fermentforsch.*, 1921, **4**, 302—315. Compare A., 1920, i, 777).—The presence of tyrosinase is best proved by the action of α-tyrosinase, after separation and activation with different neutral salts, on solutions of tyrosine. Characteristic colour reactions are obtained which differ with the particular salt used. By this method, the similarity of the tyrosinase in potatoes, red mushrooms, and meal-worms is established. The function of the salt is twofold: it first activates the α-tyrosinase and finally precipitates the colloidal melanin.

E. S.

General and Physical Chemistry.

Refraction of Light of Non-associated Liquids. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 323—324).—A theoretical paper in which it is shown that the value of the refractive index and the molecular refraction of non-associated liquids may be approximately calculated from the density at any given temperature and the critical density together with the latent heat of vaporisation and the ebullioscopic constant. The formulæ $MR = 1{\cdot}8T_s/d_cL$, and $MR = 0{\cdot}9C/d_cT_s$ represent the relationships, and in most cases give values of MR which are in keeping with known data for non-associated liquids. The refractive index of all non-associated liquids at the critical point has the value 1·126. J. F. S.

Theory of Molecular Refractions. II. Free and Activated Valencies. GERVAISE LE BAS (*Chem. News*, 1921, **123**, 56—58; see this vol., ii, 361).—From a consideration of molecular refractions the existence of free valencies of carbon, sulphur, and nitrogen in unsaturated compounds is inferred. The common cause of the regularities observed is supposed to be the existence of displaced electrons in the unsaturation centres. Further cases of negative anomalies are cited. J. R. P.

Critical Potentials and the Band Spectra of Nitrogen. LÉON BLOCH and EUGÈNE BLOCH (*Compt. rend.*, 1921, **173**, 225—227; cf. A., 1920, ii, 402).—It has been shown (*loc. cit.*) that the positive band spectrum of nitrogen appears at a potential of about 12 volts. Using a modified form of apparatus, it is now shown that the negative band spectrum appears suddenly at a well-defined critical potential of $21{\cdot}5 \pm 0{\cdot}5$ volts. W. G.

A New Spectrum of Cæsium. L. DUNOYER (*Compt. rend.*, 1921, **173**, 350—352).—By exciting the luminosity of cæsium vapour by electromagnetic induction, the author has obtained a spectrum showing six hundred and thirty rays between $\lambda = 2250$ and 6300. The spectrum varies somewhat with the pressure of the vapour. The principal rays are tabulated. W. G.

Spectra of the Alkaline-earth Fluorides and their Relation to each other. SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 436—455).—The band spectra of the fluorides of magnesium, calcium, strontium, and barium have been photographed and measured. The measurements were made in the second order spectrum, using a grating of 10 ft. radius and 15,000 lines to the inch. The compounds were introduced along with sodium carbonate into a carbon arc of 110 volts and the edge of the arc was photographed. Nine series of bands have been found in the spectrum of magnesium fluoride. Four new series have been found for calcium fluoride in the ultra-violet, and additional heads recorded

in some of the series in the visible region. Four new series have been found in the ultra-violet for strontium fluoride, and a very weak one in the red. Series designated H_1, H_2, H_3, H_4, and attributed by Leopold (*Zeitsch. Wiss. Photochem.*, 1913, **11**, 105, 137) to strontium fluoride, and the same series termed F_1, F_2, F_3 by George (A., 1913, ii, 646), and attributed to barium fluoride, are really due to calcium fluoride, and are now termed B_2, B_2', B_2'', and B_2'''. The homologous series of the alkaline-earth fluorides have been connected by empirical equations, using the constants of the series and the molecular weights or the molecular numbers of the respective compounds. An explanation is given of the appearance of a "tail" in some of the bands, starting with their series equations. It is also shown that the difference in wave numbers of the heads and tails of the similar series is constant for the same compound, but varies from one to another in a definite way.

J. F. S.

Infra-red Spectra of Isotopes. F. W. LOOMIS (*Astrophys. J.*, 1920, **52**, 248—256).—No satisfactory explanation has been given of the magnitude of the differences observed in the spectra of lead isotopes. Much larger effects should be expected for any vibration in which two atoms or nuclei, instead of one atom and an electron, are the principal masses concerned. The infra-red absorption bands of hydrogen chloride and hydrogen bromide would, in view of the complex nature of chlorine and bromine, be expected to be doublets due to isotopes. Further, there is little doubt that the central frequency of the "fundamental" band (at 3·46 μ for hydrogen chloride and 3·91 μ for hydrogen bromide) is the frequency of vibration of the charged halogen atom and the hydrogen nucleus along their line of centres. It is now shown that the frequencies of the doublets due to isotopes should be approximately proportional to $\sqrt{(m_1+m_2)/m_1m_2}$, where m_1 is the mass of the hydrogen nucleus and m_2 that of the charged halogen atom; hence the band lines due to $HCl^{(35)}$ and $HCl^{(37)}$ should differ by 1/1330, and those due to $HBr^{(79)}$ and $HBr^{(81)}$ should differ by 1/6478. Examination of the absorption spectra of hydrogen chloride, bromide, and fluoride shows that each rotational quantum line in the first harmonic of the hydrogen chloride spectrum has on the long-wave side a satellite of less intensity, separated from it by an average measured interval of 14Å, or 4·5 wave numbers, which agrees with the calculated value of 4·3 wave numbers. These satellites are the predicted lines due to the heavier isotope. Fluorine has been shown to be pure, and the absorption spectrum of hydrogen fluoride accordingly consists of single lines. In the case of hydrogen bromide, the computed separations are smaller than for the harmonic of hydrogen chloride, and the lines of separate isotopes have not been resolved.

CHEMICAL ABSTRACTS.

Chromogenetic Properties of Sulphur and certain other Elements. OLIVER C. M. DAVIS and FREDERIC WILLIAM RIXON (*Phil. Mag.*, 1921, [vi], **42**, 259—262).—It would seem that the colour of a combination of two elements, in addition to the deter-

mining effect of the nature of the elements themselves, may possibly in a measure be associated with the energy of combination, and more particularly with that energy left unabsorbed from the gross energy of the system, which may be termed the residual energy.

J. R. P.

Rotatory Power in Crystalline Media. LOUIS LONGCHAMBON (*Compt. rend.*, 1921, **173**, 89—91).—A considerable number of substances optically active in solution showed, without exception, rotatory power in the crystalline state in the direction of their optical axes. It is considered that the rotatory power may be divided into molecular and structural components. Twelve compounds not optically active in solution were found to show this rotatory power of structure in crystalline form. The rotatory power of structure is a consequence of crystalline dissymmetry. W. G.

The Diffraction of *X*-Rays by Liquids. A. DEBIERNE (*Compt. rend.*, 1921, **173**, 140—142).—When a narrow bundle of *X*-rays passes through a liquid layer sufficiently thick for an important part of the radiation to be absorbed, there is obtained on a photographic plate an aureole with a dark central region, and in some cases two such rings are shown. The phenomenon is analogous to that produced with crystals in a confused mass or in powder. The hypothesis put forward in explanation is that each radiation is dispersed as from an interior cone, where the intensity is greatest, and a heterogeneous bundle of rays will give a series of rings the diameter of which will increase with the wave-length. The centres of diffraction in liquids may be considered as constituted by the molecules, the mutual distances of which undergo only slight variations by thermal agitation, or by particularly active atoms contained in these molecules. W. G.

Röntgen Spectrographic Investigations of Organic Substances of High Molecular Weight. R. O. HERZOG and W. JANCKE (*Zeitsch. angew. Chem.*, 1921, **34**, 385—387).—The difficulties of interpreting the Debye-Scherrer diagrams can be overcome to some extent if the crystals are arranged in the direction of a main axis, whereas the other axes are disposed indiscriminately; instead of concentric rings, a two- or four-point system is thus obtained. The necessary arrangement can be secured by the use of currents of fluid, of strong electric or magnetic fields, or by pressure, although the latter method is not invariably successful even when very high pressures are used.

The general result of the application of Röntgen diagrams to a large number of organic compounds is that which would be expected from experience in chemical crystallography. Thus, the members of the fatty acid series are divisible into two groups containing odd and even numbers of carbon atoms, and here, as in the case of the melting points, the initial members of the series behave abnormally. In some instances, saturated and unsaturated compounds (fatty and oleic acids, succinic, maleic, and acetylenedicarboxylic acids) exhibit remarkable similarities, whereas in

others (β-phenylpropionic and cinnamic acids, hydrazobenzene and azobenzene) the differences are so marked that they can scarcely be attributed solely to the absence of hydrogen atoms.

The applicability of the Röntgen diagrams to the elucidation of constitutional problems is particularly illustrated in the instance of cellulose. The dimensions of the elementary body are found to be, $7{\cdot}9 : 8{\cdot}45 : 10{\cdot}2 \times 10^{-8}$ cm. and the volume $680 \times 10^{-24}(\pm 2\%)$ c.c. Since, however, $V = 1{\cdot}64 \times 10^{-24} nM/s$ (where M = molecular weight, n = the number of molecules in the elementary body, V = its volume in c.c., and s = the density of the crystal) it follows that $n = 4{\cdot}03$. In other words, the elementary body of cellulose contains four dextrose residues. Since, however, the symmetry of the elementary body is not less than monoclinic and also the molecule does not contain pre-formed *l*-dextrose, it follows that the elementary body is composed of two equal fundamental portions, each containing two dextrose residues. Since, according to Freudenberg, cellulose is composed to the extent of 35—60% of cellobiose, a residue of the latter must be present in each fundamental portion and cellulose must be entirely built up of cellobiose residues. Assuming that the geometrical demands of the theory of crystalline structure must be fulfilled, the cellobiose residues must be linked in one of the following ways, (1) as a chain of dextrose residues,

$$\ldots C{-}C_6H_{10}O_4{-}O{-}C_6H_{10}O_4{-}O{-}C_6H_{10}O_4 \ldots,$$

these being composed of four links and not containing preformed cellobiose, (2) as rings of the type,

$$\begin{array}{l} C_6H_{10}O_4{-}O{-}C_6H_{10}O_4{-}O \\ | \qquad\qquad\qquad\qquad\qquad\quad | \\ O{-}O_4H_{10}C_6{-}O{-}{-}O_4H_{10}C_6 \end{array},$$

or (3) as internal anhydrides of cellobiose, $2(C_{12}H_{20}O_{10})$. H. W.

The Fine Structure of the X-Ray Series. D. COSTER (*Compt. rend.*, 1921, **173**, 77—79).—The author has remeasured the L spectra of the elements from tantalum to uranium. He concludes that the two lines γ_2 and γ_3 are really three. There are two lines γ_2 and γ_3 which have an almost constant difference in wave-length from tantalum to uranium, and almost the same intensity. In addition, there is a line γ_6 which forms a doublet L with β_5. It crosses the line γ_2 in platinum and gold and the line γ_3 in lead and bismuth. The difference in wave-length γ_1—γ_6 is constant from tantalum to uranium. These three lines were separated in four elements, tantalum, tungsten, thallium, and uranium. In addition, the probable existence of two new lines β_9 and β_{10} has been shown. Lines such that their frequency is the sum of the frequencies of two other lines apparently do not exist. W. G.

The Distribution of the Electrons in the Heavy Atoms. A. DAUVILLIER and L. DE BROGLIE (*Compt. rend.*, 1921, **173**, 137—139).—A further discussion of the authors' own work (this vol., ii, 421, 475) and that of Coster (preceding abstract) in which the slight difference between their scheme for the distribution of energy in the heavy atoms and that of Bohr is explained.

W. G.

Disappearance of Gas in the Electric Discharge. III. THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LONDON (*Phil. Mag.*, 1921, [vi], **42**, 227—246).—A summary of previous communications (see A., 1920, ii, 730; this vol., ii, 369), with some new experiments and a theoretical discussion of the results. Except in hydrogen, absorption of gas occurs only if there is a glow discharge, and is closely associated with the ionisation of the gas absorbed. If the area of the electrodes is small compared with the walls of the discharge tube, the latter may act as a third electrode, receiving positive ions, the charge on which is neutralised by electrons from the cathode. The reaction $2CO=CO_2+C$, which plays a predominant part in the absorption of carbon monoxide, occurs by collision of a positive carbon monoxide ion with a neutral carbon monoxide molecule, and under ideal conditions the current appears to be carried by a " semi-valent " ion. Usually this simple relation is obscured by the reversibility of the reaction, recombination of ions, and arrival of positive ions at the cathode. Similar difficulties may have rendered illusory most of the cases previously recorded of the apparent exhibition of Faraday's law in gases. Preliminary experiments with nitrogen indicate an absorption proportional to ionisation, but the reactions involved are more complex. The " clean-up " of hydrogen seems entirely independent of ionisation. A luminous discharge may be obtained, showing the many-lined spectrum, without any appreciable recombination occurring.

J. R. P.

The Resistance of Selenium. H. PÉLABON (*Compt. rend.*, 1921, **173**, 295—297).—The electrical conductivity of liquid selenium increases rapidly with rise in temperature up to its boiling point, 690°. On cooling it again, the conductivity decreases with the same velocity. The slow cooling of selenium first melted and then heated at 690° results in the production at the ordinary temperature of a grey selenium, the conductivity of which is not constant for a given temperature, but can be diminished at will by slight heating and cooling. This form of selenium does not undergo reversible transformations, its properties varying with the states through which it passes.

W. G.

The Electrical Resistance of Thallium Sulphide and Selenide. H. PÉLABON (*Compt. rend.*, 1921, **173**, 142—144).—Measurements are given showing that the electrical resistance of thallous sulphide varies considerably with the method of preparing the sample and the conditions of heating. A sample that may be considered as tempered has, as a rule, a very high resistance, which, however, varies enormously with the degree of tempering. It diminishes rapidly with rise in temperature to 205° and then rises slightly to a maximum at 220°, after which it diminishes regularly. The vassage into the liquid state is accompanied by a sudden variation in the resistance. Similar results were obtained with thallous selenide.

W. G.

Regulation of Osmotic Pressure. I. The Effect of Increasing Concentrations of Gelatin on the Conductivity of a Sodium Chloride Solution. WALTER W. PALMER, DANA W. ATCHLEY, and ROBERT F. LOEB (*J. Gen. Physiol.*, 1921, **3**, 801—807).—The conductivity of pure gelatin solutions increases with the concentration of the solutions and is independent of the hydrogen-ion concentration. The actual specific conductivity is, however, higher at that hydrogen-ion concentration when the ionisation is greater. When gelatin is added in increasing concentrations to a 0·6% sodium chloride solution, the conductivity of the solution increases with each increment at the reaction when the gelatin is highly ionised but decreases at the reaction when the gelatin is less ionised.
S. S. Z.

The Conductivity of the Solution of Cupric Ammonium Citrate compared with that of Copper Sulphate. F. BEAULARD DE LENAIZAN and L. MAURY (*Compt. rend.*, 1921, **173**, 227—229).—Comparison of the electrical conductivities of solutions of copper sulphate and cupric ammonium citrate containing the same weight of copper per litre shows that for the sulphate dissociation is complete at a dilution of 1 mg. of copper per litre whilst for the citrate it is complete at a dilution of 1 gram of copper per litre. The ionisation of cupric ammonium citrate, like that of copper sulphate, obeys the law of Arrhenius and the cupric ion is free to the same degree in the two salts. W. G.

Electromotive Force of the Iodine–Silver Element and the Heat of Formation of Silver Iodide. O. GERTH (*Zeitsch. Elektrochem.*, 1921, **27**, 287—292).—The heat of formation of silver iodide has been redetermined by the *E.M.F.* method with the object of explaining the discrepancy between the results of Fischer (A., 1912, ii, 536, 1054) and Jones and Hartmann (A., 1915, ii, 308). It is shown that the discrepancy arises from a difference in the silver electrodes used in the two cases and from the correction applied to the *E.M.F.* values. The correction, which depends on the presence of I_3' in the potassium iodide solutions employed, was found in the above-named cases by calculation. The present paper indicates how this value may be obtained experimentally. The experimental measurements of the above-named authors have been repeated and confirmed; comparison of the silver electrodes used in the two cases shows that the Fischer electrode is electrochemically purer. An attempt is made to eliminate the above-named correction by using very dilute solutions of potassium iodide in the silver–iodine elements and thereby removing the disturbing effect of the I_3'. The progressively increasing inconstancy of the elements with decreasing potassium iodide concentration makes it impossible to go beyond $N/60$. A new method, however, gives the desired results. In this, very dilute solutions of iodine are obtained without further decreasing the potassium iodide concentration. By leading nitrogen (or other indifferent gas) over cooled iodine and then into a dilute solution of potassium iodide, small concentrations of iodine are obtained which correspond

with the partial pressure of the iodine and contain very little I_3'. Using the corrections thus obtained, the observed *E.M.F.* values of the iodine–silver element were corrected and the true values obtained, and from a knowledge of A and dA/dT the heat of formation of silver iodide was calculated. The value 15,158 cal. was obtained, which, compared with 15,169 cal. (Fischer) and 14,570 (Jones and Hartmann), points to the greater accuracy of the former value. J. F. S.

Electromotive Behaviour of Aluminium. A. GÜNTHER-SCHULZE (*Zeitsch. Elektrochem.*, 1921, **27**, 293—295).—A criticism of Smits's paper (A., 1920, ii, 579) in which it is shown that the statements (i) that commercial aluminium is not coated with a thin film of oxide, and (ii) that anodically polarised aluminium has no primary oxide layer, are both opposed to all known facts. The hypothesis of Smits that in normal circumstances aluminium separates electrons only extremely slowly and that this process is greatly accelerated by charging with oxygen is shown to be untenable. Further, the production of an insulating metal layer in the electrolytic formation in aluminium is also untenable. J. F. S.

Magnetic Properties of the Alkaline-earth Metals in Combination. PAUL PASCAL (*Compt. rend.*, 1921, **173**, 144—146).—Further measurements are given in confirmation of previous work (A., 1914, ii, 97, 618) showing that the diamagnetism of the alkaline-earth metal is additive in combination as salts. W. G.

New Data in Thermochemistry. WOJCIECH SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1921, [iv], **29**, 496—499).—Combining his own results (A., 1909, ii, 862, 863, 864; 1910, ii, 187) with those of Fajans (A., 1920, ii, 469), the author deduces values for the heat of formation of any linking such as $(C-X)$ or $(H-X)$ and shows that it may be considered as made up of two parts, one part being produced by the atom $(C-)$ or $(H-)$ and the other by the atom to which it is linked. Values are calculated for carbon and the halogen atoms. It is shown that the heat produced by the atom in the formation of a compound $X-Y$ is not always equal to the heat produced by it in the formation of the simple molecule $X-X$. W. G.

The Ratio of the Densities of Liquid and Vapour. WOJCIECH SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1921, [iv], **29**, 499—507.—On the basis of the physical constants of a number of compounds as determined by different workers, it is shown that the ratio k of the density of the liquid d_e to that of the vapour d_v is a function of the relative temperature $\tau=T/T_c$ and as a first approximation does not depend on the individual properties of the liquid. Certain physico-chemical properties of liquids are considered in the light of this. W. G.

A New Constant Characterising the System Vapour–Liquid. WOJCIECH SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1921, [iv], **29**, 507—512; cf. preceding abstract).—The value of B in the equation

$B=d_e^2/T\log K$, where d_e is the density of the liquid and $K=d_e/d_v$ remains practically constant for liquids which are not associated. It shows a slight maximum at the point $T/T_c=0{\cdot}60$ to $0{\cdot}65$ and a slight minimum at the point $T/T_c=0{\cdot}85$ to $0{\cdot}90$. In the case of associated liquids, the value of B increases continually with the temperature and shows no maximum or minimum. W. G.

Atomic Volume and Molecular Volume at the Absolute Zero. RICHARD LORENZ and W. HERZ (*Zeitsch. anorg. Chem.*, 1921, **117**, 267—270).—The authors show that the relationship between the molecular volume of a compound and the sum of the atomic volumes, in connexion with the energetic considerations of the spatial lattice, is best made at the absolute zero. The atomic volumes of the alkali metals, the halogens, and their compounds have therefore been calculated for this temperature. It is shown that the molecular volume of the compound is always much greater than the sum of the atomic volumes of the constituent atoms. Taking a given metal, the contraction is greatest in the case of the fluoride and least in the case of the iodide; and for a given halogen the contraction is greatest with cæsium and least with sodium. The same rule applies in the case of the sulphates and the nitrates. The biggest contraction calculated is that in the formation of cæsium fluoride, which amounts to 60·0%. J. F. S.

True Molecular Volume of Liquid Organic Compounds and its Dependence on the Structure of the Molecule. EDGAR WÖHLISCH (*Zeitsch. Elektrochem.*, 1921, **27**, 295—301).—It is shown that a comparison of the molecular volumes of organic liquids at the boiling point gives in most cases an inaccurate representation of the true molecular volumes. More suitable, for investigations on the constitutive relationships of the true molecular volumes, is the constant b of the van der Waals's equation as calculated from the critical pressure and temperature by the equation $b_c=RT_c/8p_c$. The data, such as the molecular cross-section, obtainable from the viscosity coefficient of gaseous substances also furnish a trustworthy relationship between molecular volume and molecular structure. The data furnished by the above-named two methods are in complete agreement. Molecular refraction is just as unsuited as a basis for generalisations on the true molecular volume as is the volume at the boiling point. It is shown that in their dependence on the constitution of the molecule the true molecular volume and the apparent molecular volume are frequently diametrically opposed. J. F. S.

Negative Adsorption of Alkali Haloids by Wood Charcoal. ALWYN PICKLES (T., 1921, **119**, 1278—1280).

Chemical Reactions in Mixtures of Sols. H. FREUNDLICH and ALEXANDER NATHANSOHN (*Kolloid Zeitsch.*, 1921, **29**, 16—19).—A number of chemical reactions between similarly charged sols are described. These reactions in all probability occur between the micellæ directly. Sulphur sol prepared by Odin's method reacts

with silver sol prepared by the Carey Lea method to form silver sulphide sol, whilst arsenic trisulphide sol and silver sol react to form a silver-arsenic-sulphur compound the composition of which has not been determined. Silver sol and selenium sol react to form a sulphur-selenium sol. In the reaction between silver sol and sulphur sol a series of colour changes is passed through: brown, wine-red, violet, steel-blue, greenish-blue, greenish-brown, and finally a pale yellowish-brown. The colour changes are probably due, as in the case of the photo-chlorides, to micellæ with a varying content of silver, sulphur, and sulphide. A similar series of colour changes is observed in the reaction between arsenic trisulphide and silver sols. J. F. S.

Flocculation of Colloidal Arsenic Sulphide. Influence of the Dilution of the Electrolyte and of the Quantity of Electrolyte. A. Boutaric and M. Vuillaume (*Compt. rend.*, 1921, **173**, 229—232; cf. this vol., ii, 449).—Using a constant quantity of electrolyte and colloid the velocity of flocculation diminishes at first as the dilution of the electrolyte increases, but tends towards a limit when the dilution of the electrolyte reaches a certain value. Thus in comparing the velocities of flocculation by different electrolytes, it is necessary to ensure that in every case the electrolyte is sufficiently diluted to realise the limit curve. When the amount of electrolyte is varied but the concentration is kept constant, the velocity of flocculation increases with the amount of electrolyte used. W. G.

Protecting Colloids. X. Saponin as Protecting Colloid. I. General Colloid-chemical Investigation on Guaiacum-Saponin and Quillaia-Saponin. A. Gutbier, J. Huber, and R. Haug (*Kolloid Zeitsch.*, 1921, **29**, 19—25).—Saponin solutions when submitted to dialysis slowly pass through the parchment wall whilst at the same time an inorganic constituent slowly decreases in the residue. Ageing experiments show that the more dilute the solution, the more stable it is; thus a 1% solution deposits a small, flocculent precipitate in three days and is completely coagulated in four weeks, whilst a 0·25% solution is very stable. Viscosity experiments show that only after long keeping does the solution become more viscous, and then only very slightly. Solutions of saponin in dilute alcohol are also shown by viscosity measurements to be very stable. The viscosity of saponin solutions from 0·25% downwards is practically the same, but for stronger solutions the viscosity increases with the concentration. Heating a solution of saponin and then measuring the viscosity at the same temperature shows that the viscosity decreases regularly with increase of temperature. Boiling the solution for varying lengths of time up to twenty-four hours and then keeping it at 25° and measuring the viscosity at this temperature shows a slight decrease of viscosity followed by a slight increase with increasing amount of boiling. The addition of electrolytes, hydrochloric acid, sodium chloride, and sodium hydroxide, of various concentrations, produces no very fundamental change in solutions of saponin. J. F. S.

Protecting Colloids. X. Saponin as Protecting Colloid. II. Colloidal Gold. A. GUTBIER, J. HUBER, and R. HAUG (*Kolloid Zeitsch.*, 1921, **29**, 25—27; cf. preceding abstract).—The value of saponin as a protecting colloid has been examined in the case of gold sols. From previous work it appears that saponin should constitute an active protector in the case of suspensoids; it is shown in the present work that this is not always the case. The great tendency of saponin solutions to foam is the cause of the failure, for the colloid contained in the foam is found, after a very short interval, to have become entirely irreversible. In general, solutions of colloids in the presence of saponin are not precipitated by alcohol, but in the present case concentrated alcohol precipitates the gold and saponin as a jelly. From the various solutions examined it has been possible to obtain precipitates, some of which are reversible, containing from 2·2% to 30·77% of gold. J. F. S.

Coagulation of Dispersoid Solutions at the Interfaces of Phases. (Method of Separation into Layers and Method of Shaking.) A. YANEK (*Ann. école mines Oural*, 1919, **1**, 45—58).—Two methods were used for coagulating dispersoid solutions at the interfaces of two liquid phases: (1) by shaking them with immiscible organic solvents (benzene, chloroform, ethyl ether, and carbon disulphide) in sealed test-tubes, and (2) by pouring them into a homogeneous transparent mixture of 1 vol. of chloroform, 3 vols. of water, and 4 vols. of alcohol, or 3 vols. of benzene, 1 vol. of water, and 6 vols. of alcohol. In (2) the addition of certain dispersoid solutions at once causes the transparent mixture to become turbid like an emulsion. The degree of dispersion of the latter then gradually diminishes, until finally the homogeneous mixture separates into two layers, at the interface of which the dispersoid phase is deposited as a thin film or in the form of fine flakes. It is found that negative dispersoid solutions of auric sulphide (obtained by passing hydrogen sulphide into a solution of auric chloride), zinc sulphide (obtained by passing hydrogen sulphide into a suspension of zinc hydroxide), and cupric sulphide (similarly obtained from a suspension of the precipitate produced by ammonium hydroxide in a solution of cupric sulphate) quickly and completely coagulate by both methods. The negative dispersoid solution of gold (obtained by reducing auric chloride with phenylhydrazine) coagulates but slowly when shaken with benzene, and still more slowly when shaken with ethyl ether, but quickly and completely when shaken with carbon disulphide or chloroform, and by the second method. The positive dispersoid solutions of ferric hydroxide (obtained by slowly heating a solution of ferric chloride hexahydrate to 80°) and aluminium hydroxide do not coagulate by either method. The second method was also applied to mixtures of mutually precipitating dispersoid solutions of gold (obtained by precipitating auric chloride with tannin) and ferric hydroxide.

It was found that there is an inverse ratio between the length

of time these mixtures are capable of existing and the degree of completeness of coagulation (this degree being measured by the ratio of the amount of coagulum to the total amount of the dispersoid phase) and also an inverse ratio between the completeness of coagulation and the length of time required to complete the process. Hence there is a direct ratio between the " life " of these mixtures and the duration of the coagulation process. The " longevities " of these mixtures and the velocities of coagulation are given in tables. The coagulation by the second, and probably also by the first, method is fractional. When a washed finger is immersed in the dispersoid solution of ferric hydroxide the latter behaves like a negative dispersoid solution both in (1) (shaken with chloroform) and (2). The same takes place when (1) is carried out not in sealed tubes, but in tubes closed with a washed finger. CHEMICAL ABSTRACTS.

Flame as Example of a Stationary Dispersoid System. P. P. VON WEIMARN (*Ann. école mines Oural*, 1919, **1**, Part 2, 5—6).—A flame represents a " stationary " not " stable " dispersoid system because in a stable system the particles do not change, whilst in a flame they constantly disappear, but are constantly renewed. The deposition of soot is likened to the coagulation of colloidal flakes, both being due to a concentration of particles exceeding the concentration which corresponds with the stationary state. The luminosity of a flame is most probably a function of the degree of dispersion of the dispersoid part of the stationary system. Whether the maximum of the former corresponds with the maximum of the latter is an experimental problem.

CHEMICAL ABSTRACTS.

The Equilibrium, Hydrofluoric Acid–Sulphuric Acid–Fluorosulphonic Acid. WILHELM TRAUBE and EMIL REUBKE (*Ber.*, 1921, **54**, [*B*], 1618—1626).—In previous communications (A., 1913, ii, 947; 1919, ii, 364) the unexpected stability of fluorosulphonic acid in the presence of water has been emphasised. It is now shown that equilibrium exists between sulphuric and hydrofluoric acids on the one hand and fluorosulphonic acid and water on the other in not too dilute aqueous solution. Reaction can only be partly represented by the scheme $H_2SO_4+HF \rightleftharpoons H{\cdot}SO_3F+H_2O$; a fuller account of the causes of the discrepancies is promised for a subsequent communication.

The formation of fluorosulphonic acid from hydrofluoric acid (62%) and sulphuric acid (94%) is readily demonstrated by treating the mixed acids with an excess of barium hydroxide, filtering, and treating the filtrate with acetic acid and nitron acetate, whereupon *nitron fluorosulphonate*, pale green needles, m. p. 225°, is precipitated.

The rate of decomposition of fluorosulphonic acid by water is estimated by agitation of a solution of the acid in nitrobenzene with water, filtration of aliquot portions of the solution after definite intervals of time, and precipitation of barium fluoride and sulphate in the alkaline filtrate; after removal of the precipitate, the filtrate

is acidified with hydrochloric acid and boiled, and the barium sulphate which is thereby precipitated is weighed. The total acid present in the solution is simultaneously estimated. Under these conditions and at atmospheric temperature, fluorosulphonic acid is found to be completely but very slowly hydrolysed. In this manner, it is only possible to work with small concentrations. In order to obtain more concentrated solutions and to avoid loss of hydrogen fluoride due to the heat evolved by mixing the components, fluorosulphonic acid, cooled to $-20°$, is very cautiously treated with similarly cooled ice; in these circumstances complete hydrolysis is avoided and the establishment of an equilibrium is definitely proved.

The course of the reaction can also be followed by titration with alkali since the formation of fluorosulphonic acid in accordance with the scheme $H_2SO_4+HF=H\cdot SO_3F+H_2O$ takes place with diminution of the acid titre. H. W.

Simultaneous Reactions of the Same Probability. F. E. C. SCHEFFER (*Rec. trav. chim.*, 1921, **40**, 477—487).—When a reaction is effected in n degrees and for each degree the transformation affects identical atoms or groups of atoms in identical conditions, the concentrations of the original substance and of the products of transformation successively formed are to one another as the terms of a binomial series of the nth degree. The product of the concentrations of the initial and final substances is equal to the product of the concentrations of the intermediate substances. W. G.

The Nitration of the Phenyl Carbonates. (MLLE) J. M. A. HOEFLAKE (*Rec. trav. chim.*, 1921, **40**, 488—518).—The ternary melting-point diagram of the three isomeric nitrophenyl carbonates is given, and it is shown that in the presence of a trace of alkali as a catalyst an equilibrium is set up in the molten material conforming to the equation $2\cdot o:p \rightleftharpoons o:o+p:p$, the letters indicating the positions of the nitro-groups. Based on the ternary diagram and a binary curve of fusion for the $o:o$- and $p:p$-isomerides, the author has devised a method of analysis of the products of nitration of phenyl carbonate. From the results obtained it is shown that this reaction satisfies, as a first approximation, Scheffer's formula (preceding abstract). It follows that the two phenyl groups in the carbonate do not influence the reactions of one another. This was confirmed by a study of the nitration of the mononitrophenyl carbonates. W. G.

Studies on Hypophosphorous Acid. III. Its Reaction with Mercuric Chloride. ALEC DUNCAN MITCHELL (T., 1921, **119**, 1266—1277).

Mutual Reaction of Oxalic Acid and Iodic Acid. III. Influence of Bright Sunlight. GEORGES LEMOINE (*Compt. rend.*, 1921, **173**, 192—197; cf. this vol., ii, 100, 500).—Sunlight accelerates the interaction of oxalic and iodic acids. For a given temperature the time of half decomposition in sunlight

is only about 0·4 times that in darkness. The same velocity of decomposition is obtained in sunlight at a temperature 7° lower than that in darkness. W. G.

The Rôle of the Activity Coefficient of the Hydrogen-ion in the Hydrolysis of Gelatin. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1921, **3**, 715—743).—When the hydrogen-ion concentration is kept constant, the hydrolysis of gelatin proceeds during the first part of the reaction according to the formula of a unimolecular reaction. This is most probably due to the fact that the simpler products of decomposition are more resistant to hydrolysis than gelatin itself. When, however, the hydrogen-ion concentration is not kept constant, the amount of hydrolysis in certain ranges of acidity is proportional to the square root of the time (Schütz's rule). The velocity of hydrolysis is independent of the gelatin concentration and is a function of the hydrogen-ion concentration, but not of the total amount of acid present. It is directly proportional to the hydrogen-ion concentration as determined by the hydrogen electrode. Neutral salts which increase the hydrogen-ion concentration also increase the velocity of hydrolysis to approximately the same extent. Between P_H2 and P_H10 the velocity of hydrolysis is almost constant and is very much greater than would be expected from the concentration of the respective ions. In strongly alkaline solutions the rate of hydrolysis is directly proportional to the hydroxyl-ion concentration. S. S. Z.

Catalytic Reduction of Ethylene to Ethane. DOROTHY MURIEL PALMER and WILLIAM GEORGE PALMER (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 402—412).—The rate of combination of hydrogen and ethylene in the presence of finely divided nickel has been measured at temperatures from 73° to 119°. The catalyst was deposited on clay balls which were caused to roll backwards and forwards in the reaction mixture. The method of measurement was static, the rate of reaction being deduced from the rate at which the gas mixture had to be added to keep the pressure constant. The curves showing the change of reaction velocity with time indicate an induction period, varying from a few seconds to three hours, during which there is practically no reduction. This is followed by a very rapid increase in reaction velocity to a sharp maximum, and finally the velocity falls away rapidly to a nearly steady value. The shape of the velocity–time curves is explained on the following hypothesis. Hydrogen is selectively adsorbed on nickel from mixtures of all the compositions studied whilst ethylene is adsorbed only after activation (chiefly by thermal contact with a molecule undergoing hydrogenation). On bringing the gas mixture into contact with the nickel, this becomes at once covered almost completely with hydrogen, only a few ethylene molecules being present in the adsorption layer; reaction with the formation of ethane takes place with these and the adsorbed hydrogen. The heat liberated in the hydrogenation is at once communicated to the molecules surrounding the hydrogenated molecule, leading to volatilisation of hydrogen and activation followed by

condensation of ethylene. The relative amounts of hydrogen and ethylene adhering to the surface of the catalyst thus change rapidly, once a number of centres of reaction have developed. The induction period is reduced in a very marked way either by increase of the ethylene content in the gas mixture or by increase in temperature, whilst the rate of reaction after the maximum has been passed is only very slightly affected by temperature. J. F. S.

The Influencing of Catalysts and Specifically Active Catalysts. E. ABEL (*Ber.*, 1921, **54**, [*B*], 1407—1409).—A criticism of some of the theories advanced by Rosenmund and Zetzsche (this vol., ii, 320, 392, 393). H. W.

Catalytic Activity of Copper. II. WILLIAM GEORGE PALMER (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 412—425; cf. A., 1920, ii, 609).—A continuation of previous work. In the present work the activity of copper, prepared at temperatures from 251° to 156°, on the decomposition of anhydrous ethyl alcohol and *iso*propyl alcohol containing 12% of water has been investigated. The copper catalyst was prepared by the reduction of copper oxide by carbon monoxide and by the vapour of methyl alcohol respectively. The results show that the activity of the catalyst does not necessarily increase continuously as the temperature of preparation from the oxide is lowered. The order of activity of the catalyst, reduced at various temperatures, is (*a*) carbon monoxide reduction, 215°, 229°, 194°, 243°; (*b*) methyl alcohol reduction, 251°, 225°, 217°. This result conflicts with the view that the real catalytic agent is an oxide of copper dissolved in reduced copper, but it can be readily reconciled with the hypothesis previously advanced (*loc. cit.*), namely, that the metallic copper produced by the reduction of cuprous oxide is the active agent. J. F. S.

Relation between the Occlusive Power of Palladium for Hydrogen and its Activity for Catalytic Hydrogenation. EDWARD BRADFORD MAXTED (T., 1921, **119**, 1280—1284).

The Velocity of Reaction in Hydrogenations by Platinum Black. G. VAVON (*Compt. rend.*, 1921, **173**, 360—362).—From a study of the velocity of hydrogenation of various mixtures of two substances it is shown that the part played by the solvent is important and that the rapidity with which the substance formed is removed from the catalyst has an important influence on the velocity of reaction. W. G.

Variations Produced by Stabilisers in the Catalytic Power of Electrosols of Platinum. A. DE GREGORIO ROCASOLANO (*Compt. rend.*, 1921, **173**, 234—236; cf. this vol., ii, 498).—In continuation of previous work (*loc. cit.*) it is shown that the presence of stabilisers causes a diminution in the catalytic power of electrosols of platinum. In the case of sodium protalbate, however, when the amount of stabiliser added was increased a point was reached at which the catalytic power also increased, but this was really a secondary effect due to the strongly alkaline reaction of this stabiliser. W. G.

Stability Relationships of Platinum-Organo-Sols. JOHS. LINDEMAN and THE SVEDBERG (*Kolloid Zeitsch.*, 1921, **29**, 1—16; cf. A., 1907, ii, 535; 1908, ii, 364).—The stability and size of the particles of platinum sols in ethyl ether, ethyl alcohol, and mixtures of the two have been investigated. It is shown that platinum amicrons may be gilded when the dispersion medium is ethyl alcohol or a mixture of ethyl alcohol and ethyl ether. The average radius of the amicrons can then be determined if the radius of the gilded particles is ascertained by sedimentation. Should the dispersion medium contain ether, the sedimentation must be carried out in closed vessels, for the evaporation of the ether hinders the process. The stability relations of the platinum sols in ether–alcohol mixtures have been examined by experiments on the size of the particles and by observations on the coagulation temperature. It is shown that these sols are never quite stable, but always tend, generally spontaneously, to complete coagulation. The age of these sols is determinative of their characteristics. The temperature, platinum concentration, and ether concentration appear to influence independently of one another the migration of the particles, in the sense that the velocity increases when one or more of these factors increases. The conception "Critical Temperature" of such a sol cannot be maintained in its original form, since it gives no upper temperature limit for the existence of the sols. The coagulation temperature depends much more on the velocity with which the temperature of a sol must be raised. It is preferable, therefore, to speak of the "critical curve" of a sol. J. F. S.

The Energetic Foundations of the Atomic Theory. G. URBAIN (*Bull. Soc. chim. Belg.*, 1921, **30**, 185).—A lecture delivered before the Belgian Chemical Society on June 26th, 1921.

A. A. E.

Periodic Table. A Modification more in accord with Atomic Structure. IVAN D. MARGARY (*Phil. Mag.*, 1921, [vi], **42**, 287—288).—The inert gases of the helium group are placed at the end of the series instead of at the beginning. J. R. P.

Latent Polarities of Atoms and Mechanism of Reaction, with Special Reference to Carbonyl Compounds. ARTHUR LAPWORTH (*Mem. Manchester Phil. Soc.*, 1920, **64**, (iii), 1—16).—A group such as NH_2 which tends to lower the acidity of a molecule is called "basylous"; one such as $CH_3{\cdot}CO$, which has the opposite effect, is called "acylous." The groups NH_2, NHAlk, etc., are basylous, but almost invariably exhibit negative polarity when attached to carbon; H is basylous and usually positive; CO, SO_3H, and NO_2 are strongly acylous and usually positive; whilst OH, OAlk, etc., are acylous and negative. Halogens are acylous and normally negative, but positive when contrasted with OH or NH_2. Compounds containing positive acylous groups yield acids by union with negative hydroxyl (for example, $CH_3{\cdot}CO$), and those with negative basylous groups (for example, NH_2) yield bases with positive hydrogen (or $\overset{+}{H}+H_2O$). Atoms in reactive

molecules may be labelled with + or − signs, although these are not intended to denote electrical charges, but merely indicate the relative polar characters which the two atoms seem to display at the instant of chemical change. Thus, the addition of electrolytes to the carbonyl group invariably proceeds as if the carbon atom were more positive than the oxygen atom, and selected the negative ion:

$$>\overset{+}{\mathrm{C}}\!:\!\overset{-}{\mathrm{O}}+\overset{-}{\mathrm{CN}}\cdot\overset{+}{\mathrm{H}} \longrightarrow >\mathrm{C(CN)}-\mathrm{OH}.$$

The aldol reaction, in which compounds containing the groups $>\mathrm{CH\cdot CO}-$, $>\mathrm{CH\cdot NO_2}$, $>\mathrm{CH\cdot CN}$, etc., replace HCN above, suggests an enhanced positive polar character of the hydrogen atom relative to the carbon atom on which it is situated; this is indicated as follows:

$$\begin{array}{l}\quad\overset{+}{\mathrm{H}}\\ \quad | \\ >\underset{-}{\mathrm{C}}-\underset{+}{\overset{|}{\mathrm{C}}}=\underset{-}{\mathrm{O}}\end{array}$$

Evidence for the existence of latent polarisation in the two carbon atoms is adduced. The carbonyl group, therefore, tends to develop alternate − and + polarities in a chain of atoms. The order of alternating latent polarities is determined by the oxygen atom or atoms; in nitriles by the nitrogen atom. The "key-atom" is indicated by the addition of a dot to the sign of polarity:

$$\underset{+}{\mathrm{C}}-\underset{-}{\mathrm{C}}-\underset{+}{\mathrm{C}}=\underset{\underset{\bullet}{-}}{\mathrm{O}} \qquad \underset{+}{\mathrm{C}}-\underset{-}{\mathrm{C}}-\underset{+}{\mathrm{N}}\equiv\underset{\underset{\bullet}{-}}{\mathrm{O_2}}$$

$$\underset{+}{\mathrm{C}}-\underset{-}{\mathrm{C}}-\underset{+}{\mathrm{S}}\equiv\underset{\underset{\bullet}{-}}{\mathrm{O_2}} \qquad \underset{+}{\mathrm{C}}-\underset{-}{\mathrm{C}}-\underset{+}{\mathrm{C}}\equiv\underset{\underset{\bullet}{-}}{\mathrm{N}}$$

Bivalent oxygen and tervalent nitrogen (negative) are much more effective in producing such alternations of polarity than halogens, and the influence of the oxygen is usually greater than that of the nitrogen. A perceptible influence of the opposite kind seems to be exercised by hydrogen; carbon and quinquevalent nitrogen appear to be nearly indifferent. The extension of the influence of the key-atoms over a long range requires for its fullest display the presence of double bonds, usually in conjugated positions. The above rule is called the "principle of induced alternate polarities."

Markownikoff's rule is readily explained:

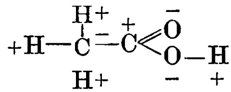
$$\overset{-}{\mathrm{X}}_1\,.\,\overset{+}{\mathrm{Y}}_1+\underset{-}{\mathrm{C}}=\underset{+}{\mathrm{C}}-\underset{\underset{\bullet}{-}}{\mathrm{X}} \longrightarrow \overset{+}{\mathrm{Y}}_1-\underset{-}{\mathrm{C}}-\underset{+}{\mathrm{C}}<^{\overset{-}{\mathrm{X}}_1}_{\underset{-}{\mathrm{X}}}$$

$$\overset{-}{\mathrm{X}}_1\,.\,\overset{+}{\mathrm{Y}}_1+\underset{+}{\mathrm{C}}=\underset{-}{\mathrm{C}}-\underset{\underset{\bullet}{+}}{\mathrm{Y}} \longrightarrow \overset{-}{\mathrm{X}}_1-\underset{\cdot\,+}{\mathrm{C}}-\underset{-}{\mathrm{C}}<^{\overset{+}{\mathrm{Y}}_1}_{\underset{+}{\mathrm{Y}}}$$

Heterogeneous arrangements arise when two isodynamic phases of the molecule can be induced by different key-atoms:

$$(A)\ \underset{\underset{\bullet}{+}}{\mathrm{H}}-\underset{-}{\mathrm{C}}\lessgtr^{\mathrm{O}}_{\underset{+}{\mathrm{O}}-\mathrm{H}} \qquad (B)\ \underset{-}{\mathrm{H}}-\underset{+}{\mathrm{C}}\lessgtr^{\mathrm{O}}_{\underset{\underset{\bullet}{-}}{\mathrm{O}}-\underset{+}{\mathrm{H}}}$$

In *homogeneous* arrangements the effect is the same no matter which of the oxygen or hydrogen atoms is regarded as the key-atom (for example, acetic acid; ethyl acetoacetate):



Halogens in the α-position behave as positive, those in the β-position as negative, groups. The relative acidities of the three isomeric cresols is explained. The principle of induced alternate polarities is considered in conjunction with free, partial, and latent valencies, and conjugation. Reference must be made to the original for schemes of reaction illustrating the application of these principles. J. R. P.

The Conjugation of Partial Valencies. ROBERT ROBINSON (*Mem. Manchester Phil. Soc.*, 1920, **64**, (4), 1—14).—The hypothesis previously described (T., 1916, **109**, 1029, 1039; 1917, **111**, 958; 1918, **113**, 639; 1919, **115**, 943) is applied to various types of chemical reactions of carbon compounds. J. R. P.

Universality of any Given State as a Consequence of the Fundamental Law of Energetics. P. P. VON WEIMARN (*Ann. école mines Oural Institute*, 1919, **1**, Part 2, 1—3).—Accepting Ostwald's view that matter is merely a spatial aggregation of different varieties of energy, and in view of the fundamental law that these varieties are mutually convertible, the author draws the conclusion that it ought to be possible to convert the chemical elements into one another, the problem reducing itself to finding the conditions for realisation of any given state. Thus, under the sodium state all elements should change to sodium; under the gold state they should change to gold, etc. CHEMICAL ABSTRACTS.

A Rotary Burner. W. VON HEYGENDORFF (*Zeitsch. angew. Chem.*, 1921, **34**, 359—360; cf. Lockemann, this vol., ii, 447).—The burner consists of a hollow drum mounted on the leading-in tube for the gas as a pivot. The top surface of the drum is provided with six holes closed by screw plugs and arranged spirally. According to the size and shape of the vessel to be heated, any number of these plugs are replaced by bunsen or other suitable burners. The lower half of the drum is filled with glycerol, which acts as a liquid seal during the rotation, which is effected by means of a small motor and a driving wheel, affixed to the lower stem of the drum. A. R. P.

Inorganic Chemistry.

New Revision of the Density of Oxygen Gas. E. MOLES and F. GONZALEZ (*Compt. rend.*, 1921, **173**, 355—358).—The oxygen used was prepared from potassium permanganate, potassium chlorate, mercuric oxide, or silver oxide, or electrolytically; and the mean of forty-five determinations gave the value 1·42889 as the density of oxygen at 0° and 760 mm. W. G.

The System, Bromine–Tellurium. The Nature of Tellurium Sub-bromide. A. DAMIENS (*Compt. rend.*, 1921, **173**, 300—303).—Using the physico-chemical methods previously applied to the system, iodine–tellurium (this vol., ii, 110, 257), it is shown that tellurium sub-bromide, $TeBr_2$, exists in the gaseous state, but is unstable in the solid state. It is an endothermic substance starting from tellurium and its tetrabromide. W. G.

Apparatus for the Preparation of Small Quantities of Pure Nitrogen or Carbon Monoxide. H. P. WARAN (*Phil. Mag.*, 1921, [vi], **42**, 246—249).—An arrangement is described for dropping one liquid into another for the generation of a gas. Nitrogen is prepared by dropping bromine water into ammonia, and carbon monoxide by dropping formic acid into concentrated sulphuric acid, both gases being dried by phosphoric oxide. J. R. P.

The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia. EUGÈNE DECARRIÈRE (*Compt. rend.*, 1921, **173**, 148—151; cf. this vol., ii, 503).—Acetylene in small amounts in the gaseous mixture causes a slight rise in the yield during the first few minutes in the catalytic oxidation of ammonia, but this is speedily followed by a drop in the yield. This drop in the yield is proportional to the absolute amount of the impurity which has passed rather than to its actual proportion, and continues even when the proportion passing is decreased or removed. The presence of hydrogen sulphide along with the acetylene in the proportion of 1 : 9 by volume apparently neutralises the influence of the acetylene alone. The initial rise is obtained, but there is no appreciable diminution in the yield. W. G.

Glow of Phosphorus. Periodic Luminosity, and Action of Inhibiting Substances. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 372—384).—The intermittent or periodic luminosity observed in a gas space when the last traces of oxygen are being removed by means of phosphorus, or when air is allowed slowly to leak into an exhausted vessel containing phosphorus, has been investigated. It is shown that this effect, as ordinarily observed, requires the presence of water vapour. Moderate drying, for example by sulphuric acid, makes the glow perfectly steady. Water vapour has therefore the power of inhibiting the combination of phosphorus vapour and oxygen within certain limits. When the

composition of the mixture becomes favourable beyond those limits, a wave of combustion is propagated. Other substances are known to inhibit the glow of phosphorus, and some of these can be used to exhibit the above-named phenomena in a far more striking form than water. Among the substances examined are camphor, pear oil (mainly amyl acetate), turpentine, ammonia, oils of aniseed, lavender, peppermint, eucalyptus, and cinnamon, nitrobenzene, butyl alcohol, amyl nitrite, and oil of bitter almonds. Of these, camphor, ammonia, and pear oil are the most effective, and experiments with them are described in detail. It is shown that the propagation of the waves of combustion cannot be attributed to the rise of temperature of one layer igniting the next layer, for the rise of temperature is too small. An alternative hypothesis of the propagation is proposed, which assumes that it depends on the provision of nuclei, as in the propagation of crystallisation through a supercooled liquid. On the basis of this hypothesis, the action of inhibitors (negative catalysts) is considered and explained. J. F. S.

The Fixation of Carbon Monoxide Diluted and Carried Along by a Current of Air. DESGREZ, GUILLEMARD, and HEMMERDINGER (*Compt. rend.*, 1921, **173**, 186—188).—The only satisfactory reagent found by the authors consisted of 70 grams of iodic anhydride, 18 c.c. of sulphuric acid (*d* 1·817), and 85 grams of granulated pumice. This mixture oxidised the whole of the carbon monoxide at a concentration of 8 parts per 1000 of air, the mixture passing at the rate of 7 litres per minute at a temperature of 35°. W. G.

Action of Sodium Amalgam on Carbon Tetrachloride. BRUNO FETKENHEUER (*Zeitsch. anorg. Chem.*, 1921, **117**, 281—282).—On warming carbon tetrachloride with 1% sodium amalgam a vigorous reaction sets in, which, investigation shows, is to be represented by the equation $4Na+CCl_4=4NaCl+C$. The reaction is quantitative, and after the initial heating completes itself quantitatively without further heating. J. F. S.

Formation of Twins in the Surface Layers of Metals during Cold Working. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1921, **117**, 271—280).—It is shown that during the polishing or shearing of plastic metals and alloys, the surface is changed to a definite depth, a fact which must be taken into account when investigating the characteristic structure of metals. It is shown that on etching a section the appearance of a twin-hatching is not the characteristic of the unworked metal, but the property of a thin surface layer which has been subjected to a cold local working, and on warming the material, undergoes a recrystallisation and disappears. The formation of the twins is explained as follows: the particles of the polishing material cut furrows in the surface of the metal and the material thus removed is pushed to either side, where it is not in equilibrium with the general orientation of the mass, and therefore a recrystallisation occurs. J. F. S.

Crystal Structure of Silver Haloids. R. B. WILSEY (*Phil. Mag.*, 1921, [vi], **42**, 262—263).—The crystal structures of silver chloride, bromide, and iodide were determined by the powder method. Silver chloride and bromide each gave the pattern of a simple cube of sides 2·78 Å.U. and 2·89 Å.U., respectively. The density of the elementary cube shows that one atom is associated with each point of the cubic lattice. Silver iodide gave the diffraction pattern of the diamond lattice, in which each side of the elementary cube was 6·53 Å.U.; one atom is to be ascribed to each point in the structure. Each iodine atom is at the centre of a tetrahedron the corners of which are occupied by four silver atoms, and each silver atom is surrounded by four iodine atoms in the same manner, the distance apart of the nearest atomic centres being 2·83 Å.U. The precipitated haloids were used; the flocculent precipitates are thus shown to be crystalline. Powdered fused silver bromide gave the same pattern as the precipitated salt. J. R. P.

The Highest Oxides of Calcium and Barium. WILHELM TRAUBE and WALTER SCHULZE (*Ber.*, 1921, **54**, [*B*], 1626—1644).—The formation of yellow products by the treatment of alkaline-earth peroxides with hydrogen peroxide has been fairly frequently recorded in the literature, but the substances have not hitherto been subjected to an extended examination. Evidence is now brought forward which points to the existence of tetroxides of calcium and barium, the former of which is considerably the more stable.

The preparation of the calcium compound is usually effected by gently warming calcium peroxide octahydrate with five to six times its quantity of pure hydrogen peroxide (30%) until a vigorous evolution of oxygen occurs; the product is removed from the source of heat until the evolution of gas subsides and the warming and cooling are repeated until practically no more gas is evolved. The precipitate is washed successively with water, alcohol, and ether and dried. The preparations have a bright yellow colour and can be heated at 130° without change in this or other property. They all show the property of dissolving in acid with a more or less brisk evolution of gas and the natural production of hydrogen peroxide; the gas consists of oxygen mixed with small amounts of carbon dioxide. The quantity of the former in the best preparations amounts to 2·7% of the weight of the substance. The evolution of oxygen is a primary action and not dependent on the decomposition of liberated hydrogen peroxide, since it occurs under conditions which do not cause evolution of gas from calcium peroxide octahydrate if it has not assumed a yellow colour. The evolved oxygen is inactive, since bromine is not liberated when the evolution takes place in an acidified solution of potassium bromide and iodine is only slightly displaced from acidified potassium iodide solution. The only known types of substance which evolve inactive oxygen are the oxyhydroxides, for example, $(KOH)_2O_2$, and the tetroxides, for example, K_2O_4. The stability of the present substance towards heat excludes the first method

of formulation, so that it is to be regarded as calcium tetroxide, CaO_4; as judged by the amount of oxygen evolved, this substance is present to the maximum extent of 8·7% in the various preparations. A typical specimen contained calcium tetroxide (5·96%), calcium peroxide (88·38%), calcium carbonate (1·98%), calcium hydroxide (2·87%), water (0·66%).

The formation of calcium tetroxide occurs, but to a considerably less extent, when calcium peroxide octahydrate is treated with water alone at 100°, its production depending on the reaction $CaO_2+2H_2O \rightleftharpoons Ca(OH)_2+H_2O_2$. Its presence also accounts for the faint yellow coloration of specimens of calcium peroxide octahydrate which have been dried at 100° or in a vacuum at 0°; an almost colourless substance can be secured only when desiccation is effected at 0° in a non-exhausted desiccator over sulphuric acid, and it is remarkable that such specimens are not transformed into the tetroxide by treatment with hydrogen peroxide.

Barium tetroxide is much less stable than the calcium compound. The substance, BaO_2,H_2O_2, can only be preserved (and even then not for extended periods) at temperatures below 0°. At the atmospheric temperature it speedily becomes yellow owing to formation of the tetroxide, and the colour increases in intensity during twenty-four to thirty-six hours, after which it disappears almost completely within four or five days, reaction proceeding according to the scheme $2BaO_2,H_2O_2=2BaO_2,H_2O+O_2$. The process occurs much more rapidly at 50—60°. If the highly coloured preparations are dissolved in acid, inactive oxygen is evolved, the amount of which corresponds with the presence of about 8% of barium tetroxide in the best preparations. The faintly coloured final products can be heated at 100° without losing the last traces of colour, which loss, however, occurs at a higher temperature with formation of anhydrous barium peroxide. The impossibility of isolating purer specimens of barium and calcium tetroxide by the present method is caused by the ready decomposability of the products in the presence of water.

The formation of the tetroxides also takes place when the peroxides, either moistened with hydrogen peroxide or in the form of their hydrates, are exposed to ultra-violet rays. H. W.

The Preparation of Calcium Carbide from Calcium Ammonium and Acetylene. L. HACKSPILL and E. BOTOLFSEN (*Compt. rend.*, 1921, **173**, 151—153).—The method of preparing calcium carbide by the action of acetylene on calcium ammonium, the product being subsequently heated to 150°, as described by Moissan (*Compt. rend.*, 1898, **127**, 911), does not give pure calcium carbide. The product when decomposed by water gave a gas containing 25% of hydrogen and 4% of ammonia, or when heated from 150—500° gave a gas containing 5% of ammonia, 20% of acetylene, and 75% of hydrogen. W. G.

Crystalline Characters of Calcium Carbide. C. H. WARREN (*Amer. J. Sci.*, 1921, [v], 3, 120—128).—Calcium carbide reveals cleavage surfaces, the cleavages being nearly equal, and parallel

to three directions at right angles to one another. The examination of cleavage fragments indicates that the carbide contains thin lamellæ which are either parallel, or inclined at 45°, to the cleavage edges. The whole structure of calcium carbide is very complex. It is considered to be of orthorhombic symmetry with a polysynthetic twinning parallel to the diagonals at 45° to the pinacoids (pseudo-duodecahedral). The twinning is mimetic, causing the carbide to appear pseudo-cubic geometrically, and pseudo-tetragonal optically. W. J. W.

Reaction of Calcium Phosphate with Sodium Carbonate and Sodium Hydrogen Carbonate. JOH. PINNOW (*Zeitsch. Elektrochem.*, 1921, **27**, 309—319).—The reaction between calcium phosphate and sodium carbonate and sodium hydrogen carbonate respectively has been examined quantitatively at 100°. It is shown that the reactions between calcium hydrogen phosphate ($CaHPO_4,2H_2O$) with sodium carbonate and disodium hydrogen phosphate in the presence of a sufficient excess of base proceed further than the formation of normal sodium phosphate when carbon dioxide is removed by passing a brisk stream of steam through the mixture. In this case, a quaternary phosphate appears in the solid phase. The quantity of carbon dioxide expelled increases, in general, with the dilution in consequence of the increased hydrolysis of the sodium carbonate. From the composition of the solutions it is shown that with a constant relationship between the components of the reaction the normal sodium phosphate content of the solid phase increases with increasing concentration, and also a portion of the sodium salt may be removed by washing the solid phase. It would therefore seem to be impossible to prepare normal calcium phosphate and calcium hydrogen phosphate free from sodium in the presence of sodium salts. The phosphoric acid content of the solid phase and the solution influence only indirectly the carbonic acid content of the solution and solid phase. The phosphoric acid content of the solid phase varies between very narrow limits and does not fall below 30% after repeated treatments with saturated sodium carbonate solution, and the calcium carbonate content never exceeds 22%. A complete separation of phosphoric acid and calcium by boiling with sodium carbonate solution is therefore impossible. J. F. S.

The Metallurgy of Zinc. LEMARCHANDS (*Rev. Metall.*, 1920, **17**, 803—811. See also A., 1920, ii, 313).—Experimental investigations of the action of carbon on zinc oxide in an atmosphere of nitrogen, the action of carbon monoxide on zinc, and the action of carbon monoxide on zinc oxide lead to the following conclusions: (1) Zinc oxide is reduced by carbon and by carbon monoxide simultaneously. (2) The reduction of zinc oxide by carbon begins at temperatures which depend on the rate of heating, being lower for rapid heating. (3) The temperature of reduction of zinc oxide by carbon is governed by the reaction velocity of the heterogeneous

system ($ZnO+C$), that is by the rate at which the two substances can diffuse and thus come into contact with each other. (4) The temperature of reduction of zinc oxide by carbon is much lower than has been previously believed, as low as 762°. (5) The reaction $ZnO+C=Zn+CO$ is reversible. It proceeds from left to right at 600°, but only at much higher temperatures is the reverse reaction noted. (6) Zinc oxide is reduced by carbon monoxide much more easily than has previously been believed, even at temperatures as low as 350—400°. (7) Values calculated on the basis of the energy liberated in the formation of these substances agree well with those found experimentally. CHEMICAL ABSTRACTS.

The so-called Action of Water on Lead. JOHN C. THRESH (*Analyst*, 1921, **46**, 270—279).—Water itself has no action on lead and merely acts as an inert medium by means of which foreign substances dissolved in it may act on the metal. Dissolved oxygen combines with the lead to form a soluble oxide or hydroxide, which remains in solution (up to saturation) unless other substances capable of combining with it are present. This solution is of a colloidal nature, and of such a coarse degree of dispersion or so liable to adsorption that it will not pass through a Pasteur filter and may even be removed by a filter-paper of fine texture. In the presence of acids yielding soluble lead salts, such salts are formed and remain in solution, but with acids yielding insoluble salts a precipitate is formed which may be deposited on the metal in such a way as to prevent further action. Any soluble salts present in the water may also act on the lead hydroxide. The whole subject is dealt with under the following headings: Effect of filtration on lead in water; factors affecting the colorimetric estimation of lead; influence of heat and agitation on the solution of lead; influence of surface area; action of distilled water; rate of utilisation of oxygen; effect of carbon dioxide; influence of carbonates. In the colorimetric estimation of lead by means of hydrogen sulphide, the best results are obtained in acetic acid solution, especially with acetic acid containing gelatin. W. P. S.

The Interpenetration of Solids. H. WEISS and P. LAFITTE (*Compt. rend.*, 1921, **173**, 146—148).—In continuation of previous work (A., 1920, ii, 545) it is shown that in the interpenetration of zinc and copper there is no discontinuity for the penetration of zinc into copper at the melting point of zinc. This result is confirmed by experiments with tin and copper, and mercury and copper. Penetration occurs at temperatures considerably below the melting point of either of the metals if sufficient time is given.

There is very appreciable penetration of zinc or tin into copper at 100° during one month. Experiments, at temperatures in each case slightly below the minimum melting point for the couple, on couples with copper as one metal and a large range of metals for the other, gave a positive result in every case except when aluminium was the second metal, and even in this case lack of penetration was probably due to lack of contact between the two metals. W. G.

Sodium Cuprite. ERICH MÜLLER [with (FRL) ILSE ERNST] (*Zeitsch. angew. Chem.*, 1921, **34**, 371—373).—Both cupric hydroxide and oxide, when shaken with strong solutions of sodium hydroxide, dissolve to an amount depending on the concentration of the alkali. The maximum solubility is reached at about 15·8*N*-sodium hydroxide and is about 0·4 mole of copper per litre in the case of the hydroxide and 0·05 mole in the case of the black oxide. On increasing the concentration of the alkali, the solubility suddenly falls in both cases to the same figure, and in 18*N*-solutions there is practically no copper in solution. In solutions of lower concentration than 15*N*, the stable solid phase is black cupric oxide, whilst with solutions of higher concentration it is sodium cuprite, which appears as a blue precipitate similar in appearance to cupric hydroxide, which, however, on warming the solution in which it is produced and again allowing to cool, crystallises. The crystals cannot be washed free from excess of alkali as they decompose into the black oxide in contact with an excess of water. Equilibrium diagrams are given of the system, copper hydroxide–sodium cuprite–sodium hydroxide–copper oxide, and the subject is discussed from a physico-chemical point of view. A. R. P.

Purification of Mercury. C. HARRIES (*Zeitsch. angew. Chem.*, 1921, **34**, 359).—An efficient method for the purification of mercury, especially that containing lead or tin which cannot be removed by distillation or treatment with nitric or chromic acids, is to heat the metal for several hours at 150° in a large flask whilst passing a current of air through it by means of a glass tube extending about 1 cm. below the surface. The metal is continually agitated and, when a considerable scum of oxide has collected on the surface, it is filtered and again treated by the same method. The process is repeated until no further scum forms, after which the filtered metal is distilled in a vacuum from an ordinary fractionating flask provided with a cork stopper carrying the condensation apparatus. The stopper is rendered gas-tight by smearing it with a mixture of chalk and glue or sulphite cellulose tar. The oxide scum produced in the first stage of the purification may contain a certain amount of finely-divided mercury, which is recovered as metal by digestion of the scum with hydrochloric acid. A. R. P.

Combinations of Halogenated Derivatives of Mercury and of Thallium. J. BARLOT and J. PERNOT (*Compt. rend.*, 1921, **173**, 232—234).—Mercury and thallium form a double chloride, *bromide*, and *iodide* of the type HgX_2,TlX, where X represents the halogen. The thallium may be estimated in these salts by converting them into the mixed nitrates, precipitating the thallium and mercury as sulphides, dissolving out the thallium sulphide with 10% nitric acid, and finally precipitating and weighing the thallium as thallous iodide. W. G.

The Ternary System : Ammonium Chloride–Manganous Chloride–Water. FREDERICK WILLIAM JEFFREY CLENDINNEN and ALBERT CHERBURY DAVID RIVETT (T., 1921, **119**, 1329—1339).

Iron–Carbon Alloys. RUDOLF RUER (*Zeitsch. anorg. Chem.*, 1921, **117**, 249—261).—The temperature–composition diagram of the system : iron–carbon has been further investigated in connexion with the solubility of cementite in molten iron and the perlite equilibria corresponding with the complete equilibrium between austenite, ferrite, and graphite. Experiments are described which show that cementite exists undecomposed in the molten system. Experiments on isolated cementite show that decomposition with separation of graphite commences at temperatures just above 1100°, and that it is impossible to melt this substance without decomposition. The amount of decomposition of cementite is 6·0% at 1112° and 63% at 1132°; at these temperatures the mass is not molten, but melts completely at 1164°. Time–cooling and time–heating curves have been made with iron containing 5% of carbon. A halt is observed at 734° in the heating curve, and on cooling from 772° a halt occurs at 720°. After allowing to cool to 600° and then reheating, halts were observed at 736° and 746°, and on again cooling the same halt was obtained at 720°, which after several successive treatments became 718°. The results show that the perlite transition occurs at 721° (cf. this vol., ii, 198). Since on the heating curve the halt corresponding with the stable eutectic lies 12° higher than that corresponding with perlite (746° against 734°), so will also the equilibrium temperature of the stable eutectic lie 12° higher than the transition temperature of the perlite, that is, at 733°. J. F. S.

The Retarded Solution and Premature Precipitation of Cementite in Eutectic and Hypereutectic Carbon Steels. SAUVAGEOT (*Compt. rend.*, 1921, **173**, 297—300).—From work with tool steels the author confirms the results of Portevin and Chevenard (this vol., ii, 510). In steels which are totally or locally hypereutectoid the influence of the initial state of the cementite on the temperature at which it disappears is very important. W. G.

"Caput mortuum" again. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1921, **45**, 801).—A brief historical essay on the origin of the terms "caput mortuum" and "colcothar." A. A. E.

Reaction between Iron Sulphide and Carbon Dioxide. V. M. GOLDSCHMIDT (*Tidskrift Kem.*, 1920, **17**, 215—218, 221—228).—The reaction expressed by the equation $FeS+3CO_2=FeO+3CO+SO_2$ does not take place below 630°, and a temperature of 1150° is necessary for appreciable reaction, whereas ferrous oxide is attacked by sulphur dioxide at 580°. Theoretical, as well as experimental, results demonstrate that the reaction is unlikely to possess practical value in metallurgical processes.

CHEMICAL ABSTRACTS.

Titanium. MAURICE BILLY (*Ann. Chim.*, 1921, [ix], **16**, 5—54).—A more detailed account of work already published (A., 1912, ii, 1178; 1914, ii, 281; this vol., ii, 456). W. G.

The Equilibria of Ter-, Quadri-, and Quinque-valent Vanadium in Solution in Concentrated Sulphuric Acid. V. AUGER (*Compt. rend.*, 1921, **173**, 306—308).—A solution of vanadic acid in sulphuric acid begins to decompose before the boiling point is reached. It loses oxygen, and after boiling for several hours an equilibrium is reached, two-thirds of the vanadium being reduced to the quadrivalent state, if the solution contains less than one part of vanadium per thousand. With more concentrated solutions, as soon as the reduction has commenced, vanadyl hydrogen sulphate is first deposited and then vanadyl sulphate until the concentration is reduced to 1 : 1000. In all cases, reduction is incomplete. Sulphur dioxide slowly reduces the vanadic–sulphuric acid solution. In the presence of sulphur, the reduction of quinquevalent vanadium gives at first a blue solution of the hypovanadyl salt and then at a later stage anhydrous vanadous sulphate is deposited and the solution is entirely free from vanadium.

Starting with a hypovanadic–sulphuric acid mixture as soon as the boiling point is reached, sulphur dioxide is liberated until one-third of the vanadium is oxidised and the solution contains the same volume of quadri- and quinque-valent vanadium as the solution mentioned above. W. G.

Mineralogical Chemistry.

The Origin and Chemical Structure of Coal. K. G. JONAS (*Zeitsch. angew. Chem.*, 1921, **34**, 373—374).—Polemical. The author considers that the theory of the origin of coal from the lignin and not from the cellulose portion of plants developed by Fischer and Schrader (this vol., ii, 210) is not in accordance with all the known facts, and in some cases even does not agree with their own results. A. R. P.

Formation of Fluorite at the Ordinary Temperature. W. WETZEL (*Centr. Min.*, 1921, 444—447).—Fragments of a calcareous rock (calcareous sandstone or siliceous limestone) were placed for some days in 3% hydrofluoric acid in a vulcanite vessel. The resulting small, model-like octahedra, up to 0·28 mm. across, have the characters of fluorite, except the low *d* 2·2 which is attributed to inclusions. By the action of the dilute acid on ordinary (soda-lime) glass minute octahedra are also produced, which only differ from fluorite in showing anomalous birefringence. L. J. S.

Analytical Chemistry.

Further Improvements in the Nephelometer-Colorimeter. PHILIP ADOLPH KOBER and ROBERT E. KLETT (*J. Biol. Chem.*, 1921, **47**, 19—25; cf. A., 1915, ii, 837; 1917, ii, 266).—The improvements, which are mainly designed to eliminate fatigue during the use of the instrument, are: the removal of the milled heads which operate the cups from the top to the bottom of the instrument; the provision of a 50 mm. auxiliary scale which can be read from the top of the instrument through an eye-piece of the same focal distance as the telescope; and the presence of a micrometer arrangement for setting the zero point which can be locked in any position. E. S.

The Substitution of Turbidimetry for Nephelometry in certain Biochemical Methods of Analysis. W. DENIS (*J. Biol. Chem.*, 1921, **47**, 27—31).—The author recommends the use of the turbidimeter (cf. Folin and Denis, A., 1914, ii, 687) in place of the nephelometer on the grounds that the former method gives accurate results with fairly wide differences (50%) between the strengths of the standard and unknown solutions. It was tested in the estimation of calcium in blood by Lyman's method (A., 1917, ii, 271), of fat in blood and milk by Bloor's method (A., 1914, ii, 392), and of inorganic phosphates in blood plasma (cf. Bloor, A., 1918, ii, 452). E. S.

Estimation of the Hydrogen-ion Concentration in Water by a Colorimetric Method. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1005—1020).—In a colorimetric method the water is treated with neutral-red solution, and the tint is compared with standardised acid and alkaline solutions of the same indicator contained in two wedge-shaped tubes attached to each other by Canada balsam. By means of a movable graduated scale the value of p_H for the corresponding tint can then be read off directly. This method is preferable to the use of the hydrogen electrode. From a knowledge of the hydrogen-ion concentration and the bicarbonate content, the carbon dioxide content may be determined from $[CO_2]=[H^{\cdot}][HCO_3']/3\times10^{-7}$ (cf. this vol., ii, 409). W. J. W.

The Potentiometric Titration of Iodides by means of Permanganate. I. M. KOLTHOFF (*Rec. trav. chim.*, 1921, **40**, 532—538).—The author confirms Hendrixson's statement (this vol., ii, 411) that potassium iodide can be titrated potentiometrically with potassium permanganate in the presence of sulphuric acid. The results are very accurate even in dilute solutions, provided that the concentration of the acid is not less than $0{\cdot}13N$. The presence of bromides or chlorides considerably lowers the jump in potential at the end point, but iodide can be estimated in the presence of twice the equivalent amount of bromide or twenty times the equivalent amount of chloride. W. G.

Colorimetric Estimation of Sulphur in Cast-iron and Steel. G. MISSON (*Ann. Chim. Analyt.*, 1921, [ii], **3**, 200—201).—One gram of the sample is placed in a conical flask, 10 c.c. of benzene and 50 c.c. of hydrochloric acid are added, and the mouth of the flask is covered with a piece of filter-paper moistened with arsenious acid solution (10 grams of arsenious oxide dissolved in 30 c.c. of concentrated hydrochloric acid and diluted to 1 litre); on this paper cover are placed, in order, a piece of white felt 5 mm. in thickness, an ebonite plate, and a lead plate weighing about 500 grams. The liberated hydrogen sulphide is absorbed by the impregnated filter-paper and the yellow coloration of the arsenious sulphide is distributed uniformly over the surface. The coloration obtained is compared with those obtained from standard specimens of metal containing known amounts of sulphur. W. P. S.

Rapid Estimation of Sulphur in Urine. CH. RABAUT and A. STILLMUNKÉS (*Progrès méd.*, 1920, 50—51; *Rep. pharm.*, 1921, (3), **33**, 37—38).—Sulphur as preformed sulphate is estimated volumetrically by addition of a standard acidified solution of barium chloride, the reaction tube being centrifuged after each addition, until precipitation no longer takes place. Total sulphate (preformed + conjugate) is estimated in a like manner after boiling the urine with hydrochloric acid, the total sulphur content being similarly estimated in a clear solution of the incinerated urine.
CHEMICAL ABSTRACTS.

Estimation of Inorganic Sulphate, Total Sulphate, and Total Sulphur in Urine by the Benzidine Method. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, **47**, 59—68).—An error, which is pronounced in the case of short period metabolism experiments, is introduced in the estimation of sulphates in urine by the benzidine method (A., 1914, ii, 142, 485; A., 1916, ii, 147) owing to the solubility of benzidine sulphate in the presence of chlorides. To avoid this error a modified method is described in which phosphates are first precipitated by shaking the diluted urine with finely powdered basic magnesium carbonate after making faintly alkaline to phenolphthalein with ammonia and adding a small quantity of ammonium chloride. The filtered solution is then used for the three estimations. Excess of chloride can now be avoided (1) in the case of the inorganic sulphate, by addition of only sufficient hydrochloric acid to make the liquid acid to bromophenol-blue; (2) in the case of the total sulphate, by hydrolysing by evaporation to dryness with a small quantity of hydrochloric acid; (3) in the case of the total sulphur, by removal of excess of hydrochloric acid, after dissolving the residue of copper oxide, by evaporation to dryness instead of by neutralisation. E. S.

New Method for the Estimation of Thiosulphate in the Presence of Sulphite and Tetrathionate. ALBIN KURTENACKER and ALBERT FRITSCH (*Zeitsch. anorg. Chem.*, 1921, **117**, 262—266).—Thiosulphate may be estimated in the presence of sulphite by the following method. The mixture of the two salts is titrated in the

usual way by means of $N/10$-iodine solution; the solution is then diluted to 200 c.c., treated with phenolphthalein, and neutralised with 5% ammonia solution. The neutral solution is now treated with about 7 c.c. of 10% potassium cyanide solution and after keeping for ten to fifteen minutes the following reaction will have completed itself: $3KCN + Na_2S_4O_6 + H_2O = Na_2S_2O_3 + K_2SO_4 + KCNS + 2HCN$. The solution is acidified with 25—50 c.c. of sulphuric acid (1 : 3) and titrated with $N/10$—$N/20$-iodine solution. From the two titration values the amount of thiosulphate and sulphite may be calculated. The method gives trustworthy results, but the conditions mentioned must be strictly adhered to.

J. F. S.

Detection of Nitrogen in Organic Compounds. CONSTANTIN D. ZENGHELIS (*Comp. rend.*, 1921, **173**, 308—310).—The organic matter is mixed with a mixture of soda-lime and copper powder, the latter two being in the proportion of 2 : 1. The mixture is placed in a crucible and covered with a layer of soda-lime and copper powder. The crucible is covered with a watch glass carrying on its under-surface a drop of the formalin–silver nitrate reagent for the detection of ammonia (this vol., ii, 558) and on its upper-surface a drop of cold water. The crucible is heated on a quartz plate until drops of water begin to condense on the watch glass, when it is put on one side. The formation of a silver mirror indicates the presence of nitrogen in the organic compound. The method is very sensitive and requires but a very small amount of material, and is applicable to all types of organic nitrogenous compounds. W. G.

Gasometric Estimation of Nitrogen. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1921, **47**, 11).—The liberation of oxygen in the gasometric estimation of nitrogen (this vol., ii, 128) is due to the use of copper sulphate in the Kjeldahl digestion. Hence if this substance is omitted the removal of oxygen is unnecessary. E. S.

Micro-estimation of Nitrogen. H. LÜHRIG (*Pharm. Zentr.-h.*, 1921, **62**, 437—444).—A detailed procedure is given for the estimation of very small quantities of ammonia, protein nitrogen (by Kjeldahl's method), and nitric nitrogen (by reduction with iron). In each case the ammonia is separated by steam-distillation and collected in $N/200$-sulphuric acid; for very small quantities of ammonia it is preferable to estimate the excess of sulphuric acid iodometrically. W. P. S.

Micro-chemical Estimation of Nitrogen by Kjeldahl's Method. VLAD. STANĚK (*Zeitsch. Zuckerind. Cechoslov.*, 1921, **45**, 323—326, 335—338, 347—349).—Full working details are given of a modification of Pregl's method (*Die quantitative Mikroanalyse*, Berlin, 1917), which has given results as accurate as the ordinary Kjeldahl's method and with a great economy of reagents and time. Except for the use of a steel condenser tube the method only differs from the ordinary Kjeldahl method in quantitative respects, for example, the amount of material used may range from a few mg. upwards, digestion is carried out with 1—10 c.c.

of sulphuric acid in a flask of 25—30 c.c. capacity, the distillation flask has a capacity of 160 c.c., and $N/70$ acid is employed in the absorption flask. An electrical device for preventing irregular boiling in the distillation flask is described. [See also *J. Soc. Chem. Ind.*, 1921, Aug.] J. H. L.

A New Reaction of Ammonia. CONST. D. ZENGHELIS (*Compt. rend.*, 1921, **173**, 153—155).—The reagent is a 20% solution of silver nitrate containing 3% of a commercial solution (33—37%) of formaldehyde and is prepared immediately before use. The exposure of a drop of this reagent to an atmosphere containing ammonia results in the formation of a thin metallic mirror. The reaction is sensitive to 0·00000034 gram of ammonia. In applying the tests to salts the ammonia is liberated by warming with dilute alkali. W. G.

Use of "Fornitral" for the Detection and Estimation of Nitric Acid. (*Ann. Chim. Analyt.*, 1921, [ii], **3**, 207—208).—"Fornitral" consists of 2 mols. of formic acid combined with 1 mol. of *endo*-anilodiphenyldihydrotriazole. Five drops of a 10% solution of this substance yields a precipitate at once when mixed with 1 c.c. of a solution containing 0·03 mg. of nitric acid. For the estimation of nitric acid, 100 c.c. of a solution containing about 0·1 gram of nitric acid are acidified with 10 drops of dilute sulphuric acid, the mixture is boiled, and 10 c.c. of the reagent are added; the mixture is then cooled at 0° for two hours, the precipitate collected on a filter, washed with a small quantity of cold water, dried at 100°, and weighed. The weight found is multiplied by 0·168 to obtain the amount of HNO_3 present. W. P. S.

An Improved Gas Combustion Furnace for Use in Organic Analysis. THOMAS JOHNSON HEDLEY (T., 1921, **119**, 1242—1243).

Estimation of Calcium in Blood. M. KAHN and L. G. HADJOPOULOS (*Proc. Soc. Exp. Biol. Med.*, 1921, **18**, 200; from *Physiol. Abstracts*, 1921, **6**, 311).—The calcium is precipitated as oxalate, centrifuged, washed, dried, and ashed. The residue of calcium oxide is dissolved in $N/50$-hydrochloric acid and the excess of the latter titrated with $N/100$-sodium hydroxide, using phenolphthalein as indicator. C. R. H.

Estimation of Metal Sulphides by Heating in Hydrogen Sulphide. I. L. MOSER and ANNA SCHATTNER (*Chem. Zeit.*, 1921, **45**, 758—759).—Zinc, cadmium, manganese, and silver may be estimated gravimetrically by conversion into sulphide, followed by ignition of the dried compound in a current of dry hydrogen sulphide gas. The latter is prepared by the action of hydrochloric acid on ferrous sulphide, and is purified by passing it in succession through four wash-bottles maintained at 60°, and containing 1 : 2, 1 : 4, and 1 : 8 hydrochloric acid and water respectively, then through a wash-bottle containing cold water, a tube filled with potassium hydrosulphide, and lastly through a large U-tube packed with calcium chloride. The precipitated sulphides are dried, the

precipitate is detached from the paper, the latter ashed in a crucible, the main precipitate added, and the crucible supported in a Bunsen flame so that it is surrounded by about three-fourths of the flame. The crucible is covered with a perforated lid through the hole in which a glass tube, to deliver the gas, projects two-thirds of the way down the crucible. A steady stream of gas is passed through for $\frac{1}{2}$—$\frac{3}{4}$ hour while the bottom of the crucible is maintained at a dull red heat, and the gas current is kept on until the whole is quite cold. In this way the sulphides are obtained in a dense or crystalline form. By simple ignition in the above manner the following compounds may be converted into, and weighed as, sulphide—zinc oxide, carbonate, and sulphate, manganese sulphate, dioxide, and trimanganese tetroxide, silver chloride, or nitrate. If iron sulphide or oxide is treated in the above manner the residue contains higher sulphides of iron, but exact results may be obtained by diluting the hydrogen sulphide with five times its volume of hydrogen, and heating for half an hour, after which the residue is cooled in a current of hydrogen and weighed as FeS. A. R. P.

Gravimetric Analysis. XVIII. XXIII. Determination of Cadmium. L. W. WINKLER (*Chem. Zeit.*, 1921, **34**, 383—384).—On passing a current of hydrogen sulphide through a hot, strongly acid solution of cadmium sulphate containing a very small quantity of hydrochloric acid, a heavy, red, crystalline precipitate of cadmium sulphide containing 1·01% of SO_4 is obtained. A gravimetric method for the determination of cadmium based on this fact is carried out as follows. The neutral or slightly acid cadmium sulphate solution containing 0·25—0·01 gram of cadmium and about 100 c.c. in bulk, is treated with 3 c.c. of concentrated sulphuric acid and 1 drop of *N*-hydrochloric acid, heated to boiling and saturated with hydrogen sulphide for 15 minutes; then cooled to the ordinary temperature and again treated with the gas for 15 minutes. The precipitate is collected on a wad of cotton wool that has previously been washed with methyl alcohol and dried at 130°, washed with 50 c.c. of water containing a few drops of acetic acid and some hydrogen sulphide, then with methyl alcohol, dried first at the ordinary temperature, then at 130° for one hour and weighed. One mg. is added to the weight so found to allow for the cadmium that is not precipitated, and the figure is then converted to that for the pure sulphide by multiplying by 0·9806. Chlorides should be removed first by evaporation of the solution with an excess of 3 c.c. of sulphuric acid more than that necessary to decompose them. Sulphates of the alkali metals, magnesium, manganese, ferrous iron, cobalt, nickel, aluminium, or chromium do not interfere. Zinc is partly co-precipitated; in its presence, the precipitate should be re-dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, the mass taken up in water, and the precipitation with hydrogen sulphide repeated. A. R. P.

Estimation of Small Amounts of Lead in Brass. FRANCIS W. GLAZE (*J. Ind. Eng. Chem.*, 1921, **13**, 553—554).—In determining lead electrolytically as lead dioxide, current density and acid

concentration are the most important variables. The following method has proved satisfactory for estimating lead in amounts less than 0·06%. 8·643 Grams of a sample of brass are treated with 30 c.c. of nitric acid (1 : 1) and then dissolved by adding 10—15 c.c. of nitric acid (*d* 1·42) and warming. The solution is evaporated until cupric nitrate begins to crystallise out, cooled, and heated with 5 c.c. of nitric acid and a small amount of water until the salt redissolves. After dilution to volume, it is electrolysed at a current of *N.D.* 100 of 1·5 amperes, and 2·9—3·1 volts. Deposition of the lead dioxide is complete in one hour, but the current should be continued for a further ten minutes. The anode is washed with water and alcohol, dried at 200—230° for half an hour, cooled, and weighed. After cleaning, it is again weighed, and the difference ×10 gives the percentage of lead in the brass. W. J. W.

The Titrimetric Estimation of Mercury. EINAR BIILMANN and (MLLE) KARIN THAULOW (*Bull. Soc. chim.*, 1921, [iv], **29**, 587—592).—Two methods are described. One is based on the fact that allyl alcohol reacts with mercuric salts to give an organo-mercuric compound, $C_3H_5{\cdot}OH+HgX_2=C_3H_5{\cdot}O{\cdot}HgX+HX$, which with alkali gives a hydroxide, $C_3H_5{\cdot}O{\cdot}HgX+NaOH=C_3H_5{\cdot}O{\cdot}Hg{\cdot}OH+NaX$, which is so feebly basic that it does not redden phenolphthalein. It reacts with potassium bromide to liberate an equivalent amount of potassium hydroxide, $C_3H_5{\cdot}O{\cdot}Hg{\cdot}OH+KBr=C_3H_5{\cdot}O{\cdot}HgBr+KOH$. To an acid solution of the mercuric salt, allyl alcohol is added together with a few drops of phenolphthalein and a slight excess of sodium hydroxide. The solution is exactly neutralised with acid, five grams of potassium bromide are added, and the alkali liberated is titrated with standard acid.

For the second method the salt is dissolved in dilute acid and the solution is supposed to be free from halogen ions or carbon dioxide. A few drops of phenolphthalein are added and an excess of sodium hydroxide. Dilute sulphuric acid is added until the red colour of the indicator exactly disappears and then 5 grams of potassium iodide are added. The action occurring is $HgO+2KI+H_2O=HgI_2+2KOH$. The alkali liberated is titrated with standard acid. W. G.

The Precipitation of some of the Rare Earths by Creams of Insoluble Oxides and Carbonates, based on the Principle of Hydrolysis. ARTHUR C. NEISH and J. W. BURNS (*Can. Chem. Met.*, 1921, **5**, 69—74).—An investigation of the hydrogen-ion concentration of some salts of the rare earths, and the hydroxyl-ion concentration of various oxides and carbonates has led to the development of the following scheme of analysis : The solution is treated with hydrogen sulphide or sulphur dioxide to reduce cerium compounds to the cerous condition, excess is removed by boiling, and the solution then treated in an atmosphere of carbon dioxide with a slight excess of lead, zinc, or copper carbonate, red lead or zinc oxide, whereby thorium hydroxide is precipitated; after being dissolved and reprecipitated, this is washed, ignited, and weighed. The original filtrate is treated with a small excess of

potassium permanganate, boiled, a slight excess of lead, manganese, or zinc carbonate, or red lead added, and the mixture quickly filtered from precipitated ceric hydroxide, which is estimated as before. To the filtrate is then added a slight excess of magnesium oxide or carbonate, or silver oxide; after being heated to 60° only, the liquid is filtered; neodymium and praseodymium are separated by fractional precipitation with ammonia of the redissolved residue, whilst lanthanum hydroxide is removed from the filtrate with sodium hydroxide. CHEMICAL ABSTRACTS.

The Estimation of Small Quantities of Iron. L. MAQUENNE (*Bull. Soc. chim.*, 1921, [iv], **29**, 585—587).—For the estimation of iron in plant products the material is ashed at a red heat and 0·01—0·05 gram of the ash is moistened with nitric acid and again calcined. To the residue 1 c.c. of 10% sulphuric acid is added and the mixture heated until white fumes are evolved. Three drops of hydrochloric acid and 1 c.c. of water are added, and the liquid is decanted into a tube of 3—4 c.c. capacity. The residue is washed with 1 c.c. of water. Any calcium sulphate in the decanted liquid is removed by centrifuging it. The clear liquid is decanted and a few drops of sodium phosphate and a very slight excess of ammonia are added, until a permanent precipitate is obtained. One c.c. of acetic acid is added and the ferric phosphate, which is insoluble, is separated by centrifuging and dissolved in three drops of hydrochloric acid, the solution being diluted to 2 c.c. and poured into a tube containing a few drops of potassium ferrocyanide, the iron then being estimated colorimetrically against standards. W. G.

Estimation of Small Quantities of Iron. L. MATHIEU (*Ann. Falsif.*, 1921, **14**, 203—204; cf. this vol., ii, 351).—Under proper conditions of illumination, the thiocyanate method is trustworthy for the estimation of very small quantities of iron. In the case of wine, the ash should be dissolved by heating with 10% sulphuric acid and the solution then treated with two drops of 10% nitric acid before the thiocyanate is added. W. P. S.

Estimation of Cobalt and Nickel in Cobalt Steels. G. E. F. LUNDELL and J. I. HOFFMANN (*J. Ind. Eng. Chem.*, 1921, **13**, 540—543).—In the electrolytic method of determining cobalt and nickel, vanadium interferes in the deposition of either alone, but not when both are electrolysed simultaneously. Tungsten affects the deposition of cobalt, or cobalt and nickel, but not of nickel alone. Ferrous salts, chromates, tartrates, and molybdenum exert marked interference, but sulphates of potassium, manganese, and chromium, chlorides, and small amounts of platinum, are without harmful effect. In the following method the action of interfering agents is avoided. The steel is dissolved in hydrochloric and nitric acids, and tungstic and silicic acids are filtered off and treated with sodium hydroxide. Insoluble matter is then filtered off, dissolved in hydrochloric acid, and added to the main solution. By treatment of this with ether, most of the iron and molybdenum are removed. The acid extract is heated with sulphuric acid until fumes are

evolved, chromium, vanadium, and manganese are oxidised with potassium persulphate, and the hot solution is added to hot sodium hydroxide solution and filtered, by which process chromium, vanadium, and any residual tungsten and molybdenum are removed. The precipitate is dissolved in sulphuric acid to which a little sodium bisulphite is added, and the copper separated by treatment with hydrogen sulphide. Iron is removed by double precipitation with ammonium hydroxide after expulsion of hydrogen sulphide and re-oxidation. The combined filtrates are then electrolysed for nickel and cobalt, which are weighed and dissolved, and the nickel is finally separated by treatment with dimethylglyoxime. If desired, separate estimations may be made of chromium, vanadium, manganese, and copper isolated by the above method. W. J. W.

Reactions of the Xanthates. A. WHITBY and J. P. BEARDWOOD (*Journ. Chem. Met. Soc. S. Africa*, 1921, **21**, 199—200).—Nickel and cobalt may be separated by the use of an alkali xanthate in the following manner: The solution is treated with 1 gram of citric acid, followed by ammonia until alkaline; 1 gram of sodium or potassium xanthate is then added and acetic acid until just acid, whereby nickel and cobalt are quantitatively precipitated. After remaining in a warm place for two to three hours, the solution is filtered, the precipitate well washed with warm water, rinsed back into the original beaker, and digested with 1 : 1-ammonia to dissolve the nickel compound. The insoluble residue of cobalt xanthate is collected, washed with ammonia until all yellow colour is removed from the paper, and ignited to Co_3O_4 which is weighed. The nickel in the filtrate is recovered by acidifying with acetic acid; the precipitate is collected, washed with warm water, ignited, and weighed as NiO. Copper, if present in the original solution, is found with the cobalt fraction; it may be removed by solution of the ignited oxides in hydrochloric acid, followed by precipitation with hydrogen sulphide. A. R. P.

Estimation of Small Amounts of Chromium in Steels. B. S. EVANS (*Analyst*, 1921, **46**, 285—286).—The method depends on the red coloration obtained when chromic acid is treated with diphenylsemicarbazide solution, and is suitable for the estimation of quantities of 0·001%, or less, of chromium in iron. The reagent is prepared by dissolving 1 gram of diphenylsemicarbazide in 10 c.c. of glacial acetic acid and diluting the solution with water to 1 litre; 5 c.c. of the reagent and 10 c.c. of dilute (1 : 3) sulphuric acid are used for each test. W. P. S.

Detection of Antimony in Presence of Tin. VLADIMIR NJEGOVAN (*Chem. Zeit.*, 1921, **45**, 681).—In hydrochloric acid solutions containing antimonious and stannic chlorides, as obtained in the ordinary course of qualitative analysis, the antimony may be detected by precipitation as red oxysulphide on boiling with sodium thiosulphate solution. The stannic salt gives at the same time a white precipitate of sulphide and hydroxide. If, for example, 1 c.c. of the hydrochloric acid solution is partly neutralised with

sodium carbonate but left acid enough to prevent separation of basic salts, and then boiled for one minute with one or two drops of $N/2$-sodium thiosulphate solution, antimony may be detected even at a concentration of $N/100$ in presence of $N/2$-stannic chloride, by the pink tint of the precipitate. Excess of thiosulphate must be avoided, as the precipitation of sulphur masks the red colour. Stannous chloride, if present, should be oxidised with nitric acid before the test. Any cupric salt present is precipitated as sulphide, thus masking the reaction, and in this case the liquid should be made slightly alkaline with sodium carbonate, warmed to dissolve the antimony oxysulphide, filtered from copper sulphide, acidified with hydrochloric acid, and heated again with thiosulphate.

J. H. L.

Methods of Estimating Cholesterol and Allied Substances. John Addyman Gardner and May Williams (*Biochem. J.*, 1921, **15**, 363—375).—The estimation of coprosterol colorimetrically by means of acetic anhydride and sulphuric acid against coprosterol and cholesterol standards is influenced both by the volume of acid and by temperature. In estimating coprosterol against cholesterol, precautions ought also to be taken to avoid the difference in the time of the colour induction. ψ-Coprosterol cannot be estimated colorimetrically against either cholesterol or coprosterol. β-Cholestanol gives only a very faint colour reaction with acetic anhydride and sulphuric acid, which is most probably due to traces of cholesterol, and it cannot therefore be estimated colorimetrically. Cholesteryl acetate, benzoate, and stearate give the colour reactions as easily as cholesterol itself, but the quantitative results are rather high. With coprosteryl acetate, on the other hand, the colour changes are very slow. The presence of amorphous sterols from fæces vitiates the colorimetric estimation of cholesterol and coprosterol owing to the bright green coloration which they ultimately give. The colorimetric method cannot be applied to the estimation of the unsaponifiable matter of fæces. The ether extracts of serum or blood can be estimated colorimetrically. Results obtained with extracts from other tissues are untrustworthy.

S. S. Z.

Source of Error in the Colorimetric Methods for the Estimation of Cholesterol in Tissue Fats. John Addyman Gardner and Francis William Fox (*Biochem. J.*, 1921, **15**, 376—378).—Alcoholic potassium hydroxide on being extracted with ether yields some resinous matter which when dissolved in chloroform gives a coloration with acetic anhydride and sulphuric acid. Such a coloration is sufficient to introduce an error in the estimation of cholesterol.

S. S. Z.

Micro-estimation of Dextrose by means of Potassium Permanganate. Application to Blood and Cerebro-spinal Fluid. G. Fontès and L. Thivolle (*Bull. Soc. chim. Biol.*, 1921, **3**, 226—237).—The method is a modification of that of Folin and Wu (A., 1919, ii, 308), the estimation being made volumetrically

instead of colorimetrically. In place of the phenol reagent, a phosphomolybdic acid reagent is used. This is prepared by boiling 40 grams of ammonium molybdate with 60 c.c. of sodium hydroxide (*d* 1·36) and 100 c.c. of water until ammonia is no longer evolved; after cooling, 200 c.c. of water and 200 c.c. of phosphoric acid (*d* 1·38) are added and the solution is again boiled for fifteen minutes. The cold solution is diluted to 1 litre. For the estimation, the protein free filtrate (2 c.c.) from blood or cerebro-spinal fluid containing 0·5—1 mg. of dextrose is boiled for six minutes with an alkaline copper tartrate solution (1 c.c.). Saturated solutions of magnesium sulphate (5 drops) and sodium carbonate (4 drops) are quickly added and the solution is again boiled for one minute. The cuprous oxide precipitate, after separation by centrifuging, is dissolved in the phosphomolybdic acid reagent (5 c.c.) and the blue solution so obtained titrated with a 0·008% potassium permanganate solution until the colour is discharged. The result is calculated by comparison with 2 c.c. of a 0·05% dextrose solution similarly treated. The observed error is 3—5%. The above quantities are modified for smaller concentrations of dextrose; the error in this case is greater. E. S.

[Colour Reaction for] Lignified Cell Membranes. P. CASPARIS (*Pharm. Monatsh.*, 1920, **1**, 121—160).—Lignified cell-walls are stained blue by adsorption of a 15—40% solution of cobalt thiocyanate tetrahydrate, the reaction being considerably more sensitive than either Maeule's permanganate test or the phloroglucinol test. Maeule's test is characteristic only of lignin commonly present in angiosperms, and consists of an oxidation and a chlorination phase; thus it is closely related to the "chlorosulphite" reaction of Cross and Bevan. CHEMICAL ABSTRACTS.

Dinitrosalicylic Acid: A Reagent for the Estimation of Sugar in Normal and Diabetic Urine. JAMES B. SUMNER [with V. A. GRAHAM] (*J. Biol. Chem.*, 1921, **47**, 5—9).—A colorimetric method depending on the reduction of 3 : 5-dinitrosalicylic acid. One c.c. of 2% sodium dinitrosalicylate solution (prepared by dissolving 2 grams of dinitrosalicylic acid in water containing 10 c.c. of 20% sodium carbonate solution and diluting to 100 c.c.) and 2 c.c. of 1·5% sodium hydroxide solution are added to 1 c.c. of urine. The mixture is heated for five minutes and the amount of reduction determined by comparison with a standard in a colorimeter. To correct for the reduction due to uric acid and polyphenols, 1 c.c. of urine is heated for fifteen minutes with 1 c.c. of 3% sodium hydroxide; this destroys reducing sugars. An amount of dextrose approximately equal to that of the reducing sugars originally present is then added and the reduction determined as above. After deducting that due to the dextrose, this gives the correction to be applied. E. S.

General and Physical Chemistry.

Balmer Series of Hydrogen. E. GEHRCKE and E. LAU (*Ann. Physik*, 1921, [iv], **65**, 564—576).—The lines of the Balmer series of the hydrogen spectrum have been examined with respect to their structure, energy partition, and width. It is shown that the Balmer lines are more easily obtained in the presence of a little water. The intensity relationship of the two components is found to depend on the method of excitation and the source of light.

J. F. S.

Mass Spectra of the Alkali Metals. F. W. ASTON (*Phil. Mag.*, 1921, [vi], **42**, 436—441).—An apparatus for the production of positive rays of the alkali metals by volatilising their salts by means of a hot anode is described. The following results were obtained :

Element.	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Minimum number of isotopes . . .	2	1	2	2	1
Mass of isotopes in order of intensity .	7, 6	23	39, 41	85, 87	133

It is shown that for the great majority of the possible configurations even atomic weight is associated with even atomic number and odd with odd, which is interpreted as meaning that in the nuclei of most types of atoms the number of electrons is an even number.

J. R. P.

Quantitative Relationships of the Cæsium Spectrum. HANS BARTELS (*Ann. Physik*, 1921, [iv], **65**, 143—166).—The series law put forward by Füchtbauer and Hoffmann (*Ann. Physik*, 1914, **43**, 96) has been examined in the case of the cæsium doublet $5p$ (λ=3612 and 3617) and found to be correct within the limits of experimental error. The absorption of the strongest component (λ=3612) of the principal series doublet $5p$ has been measured and by making use of earlier measurements has been compared with the absorption of the corresponding component of the doublet $4p$. From the absorption measurements by means of the Herz vapour pressure formula $\log_e p = A + B \log_e T + c/T$, several values of the vapour pressure of cæsium have been calculated. These values are : 190·9°, p=0·046 mm., 199·2°, p=0·068 mm., 204·7°, p=0·084 mm., 232·3°, p=0·211 mm. (cf. Kröner, A., 1913, ii, 383). These values probably have a 10% absolute error, and a relative error of 4%. J. F. S.

Bergmann Series of Cæsium. K. W. MEISSNER (*Ann. Physik*, 1921, [iv], **65**, 378—392).—The vacuum arc spectrum of cæsium has been photographed and evaluated in the red and infra-red regions. Twenty-nine lines of wave-lengths 8079·021—6010·489 Å.U. are recorded, the values of which were obtained by reference to the red cadmium line $2p_2 - 4{\cdot}5s$, 6354·552 Å.U. The

measured lines are used for the investigation of the Bergmann series. It is shown that various pairs have not a constant frequency difference, but the individual components come more closely together the larger the series number, and for the series number $m=\infty$ the difference Δ^{ν}_{∞} reaches the limiting value 97·59 cm.$^{-1}$. The two limiting terms necessary to characterise the series are found to be 16809·620 ($3d_1$) and 16907·190 ($3d_2$). Making use of these limiting values, the wave-lengths calculated and observed are compared and a remarkably good agreement is obtained.

J. F. S.

Arc and Spark Spectra of the Alkalis, Alkaline Earths, and Earths. R. SEELIGER and D. THAER (*Ann. Physik*, 1921, [iv], **65**, 423—448).—The arc and spark spectra of lithium, sodium, potassium, magnesium, calcium, zinc, mercury, and aluminium have been investigated. It is shown in all these cases that the displacement law is correct in so far as all the lines of the elements may be arranged in two groups of smaller and larger exciting energy. The energy necessary for the excitation of the arc lines increases from the alkalis to the earths through the alkaline earths. The energy necessary for excitation of the arc lines of one and the same element increases in the order: Bergmann series, principal series, second subsidiary series, first subsidiary series, single line series, spark lines. The unknown form of the excitation function has considerable influence in both the above cases. It is significant that in its entire behaviour the Bergmann series, of the whole arc series, is furthest removed from the spark lines. The spark spectrum (fundamental spectrum) of sodium has been observed in the negative glow of the glow discharge. The results concerning the intensity relationships at the edge of the glow discharge show that the exciting energy of the single line series is greater than that of the remaining arc series. Vigorous evaporation of the cathode in a glow discharge is not generally sufficient to lower the cathode potential to that characteristic lower value required for the arc, but an anomalous cathode fall may be set up over a vaporising molten cathode. J. F. S.

Absorption of Light by Elements in a State of Vapour. The Halogens. (SIR) J. J. DOBBIE and J. J. FOX (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 456—461; cf. A., 1920, ii, 170).—The absorption of light by iodine and bromine vapour and by chlorine has been examined at temperatures from 22° to 1350°. When light from a Nernst filament is allowed to fall on a white screen after passing through bromine vapour at various temperatures it is found that the colour, which is deep orange at ordinary temperatures, changes to brick red at 100°, the intensity of the transmitted light diminishes at 600° and above, and the vapour is most opaque at 900°. Above this point the colour changes to orange-red; at 1200° it is pale yellow, and at still higher temperatures nearly white. The absorption increases regularly up to about 900° and then falls off continuously. The absorption band has its middle situated at about λ4170. Iodine vapour changes colour on heating,

at temperatures up to 300° the colour being reddish-violet, which deepens in shade up to 500°. At this temperature, the intensity of the transmitted light is much enfeebled and remains so to 800°, when it again increases, the violet shade becoming lighter. At still higher temperatures, the violet shade passes gradually into a bright salmon colour, and finally disappears almost entirely. The absorption increases regularly to 600°, and is much more distinctly defined than in the case of bromine. In the case of chlorine, the absorption becomes greater with increase of temperature up to 1190°, but up to this temperature no reversal is observed as in the other cases. The results are discussed in connexion with the dissociation and size of the molecules of the halogens. J. F. S.

Colorations produced by Substituted Nitroforms. HUGH GRAHAM and ALEXANDER KILLEN MACBETH (T., 1921, **119**, 1362—1368).

Criticism of Bohr's Theory of Light Emission. A. SOMMERFELD (*Jahrb. Radioaktiv. Elektronik*, 1921, **17**, 417—429).—The author supports Bohr's theory against criticisms of J. Stark (this vol., ii, 232). J. R. P.

Significance of Continuous Absorption and Emission Spectra in Bohr's Theory. R. LADENBURG (*Jahrb. Radioaktiv. Elektronik*, 1921, **17**, 430—434).—Polemical with J. Stark (see preceding abstract). J. R. P.

Luminescence of Solid Solutions. GERHARD C. SCHMIDT (*Ann. Physik*, 1921, [iv], **65**, 247—256).—The author has examined the luminescence of a number of dyes adsorbed in other material and finds that in no case is any fluorescence to be observed; on the other hand, the same dyes when in solid solution in gelatin or phthalic acid exhibit a very pronounced fluorescence. Among the dyes examined were bismarck-brown, quinoline-yellow, congo-red, ponceau-red, eosin, methylene-blue, and methyl-violet. The difference noted above can be shown with one and the same substance as solvent or adsorbent; thus benzoic acid in which methyl-violet is adsorbed shows no fluorescence, whilst when the methyl-violet is dissolved in the acid to form a solid solution a very intense yellowish-red fluorescence is observed. It is shown further that the fluorescence of fluorescein, eosin, and fluoridin in benzidine, benzoic acid, phthalic acid, acetamide, benzamide, and acetanilide is the same in both liquid and solid solutions. The adsorption of methyl-violet in benzoic acid from aqueous solution follows the partition law. The author attributes the different behaviour in the two cases to the different condition of the dye substance; in the case of adsorption, the dye lies on the surface, but in the case of solid solutions the dissolved substance lies in the crystal lattice of the solvent. The difficulty of formation of solid solutions in inorganic substances is considered and explained. J. F. S.

Active Racemic Substances. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1921, [iv], **29**, 656—669).—A discussion of the literature on

this subject, in which the author adopts the more general definition of a racemic compound as a crystalline edifice composed of molecules of dextrorotatory configuration and of lævorotatory configuration in equal numbers. Optical activity is only an accessory phenomenon dependent on the quality of each molecule. This is amplified by illustrations showing the possibility of obtaining active racemic compounds. W. G.

Temperature Coefficient of the Electrical Double Refraction in Liquids. II. C. BERGHOLM (*Ann. Physik*, 1921, [iv], **65**, 128—142; cf. *ibid.*, 1916, **51**, 414).—The temperature coefficient of the electrical double refraction has been determined, by the method previously adopted, for the liquids: toluene, *m*-xylene, carbon disulphide, chlorobenzene, bromobenzene, chloroform, ethyl ether, ethylene dibromide, and carbon tetrachloride. It is shown that the agreement between the observed and calculated values of the temperature coefficient is only qualitative. The relationship, B_{t°/B_{20°, between the Kerr constant at t° and 20° in the case of toluene and carbon disulphide is very nearly dependent on the wave-length of the light used. In the case of liquids with a more positive Kerr constant, B_{t°, the expression $B_{t^\circ}T/(\epsilon+2)^2$ is very nearly constant, ϵ being the dielectric constant at t°.

J. F. S.

New Application of Einstein's Photochemical Equivalent Law. WALTER NODDACK (*Zeitsch. Elektrochem.*, 1921, **27**, 359—364).—The photochemical reactions between bromine and *cyclo*hexane and between chlorine and trichlorobromomethane have been investigated. In the former case a slow, dark reaction takes place; in the latter no recognisable change takes place in forty days at 37°, but some reaction occurs at 100° in several hours (see this vol., ii, 580). It is shown that both reactions follow the Einstein photochemical equivalent law, the divergences observed being explained by the experimental error and by the complicated dark reaction. In the case of the reaction between chlorine and trichlorobromomethane, it is found that admixture with carbon tetrachloride lowers the photochemical effect with increasing dilution. This phenomenon is ascribed to the energy loss of the activated molecules owing to indifferent collisions with the carbon tetrachloride molecules. The illumination of the mixture: chlorine, trichlorobromomethane, carbon tetrachloride, represents a limiting case of pure photochemistry and in it the light energy is partly converted into chemical energy and partly into heat. The life of the Bohr condition has been deduced from the decrease of the photochemical effect, and is found to be approximately 10^{-9} seconds.

J. F. S.

Photographic Colloid-Chemical Crystallisation Processes. A. STEIGMANN (*Kolloid Zeitsch.*, 1921, **29**, 145—148; cf. this vol., ii, 13, 147).—A theoretical paper in which the author discusses the results obtained in previous papers (*loc. cit.*). J. F. S.

Passivity and Photo-electricity. WILHELM FRESE (*Zeitsch. wiss. Photochem.*, 1921, **21**, 37—44).—The connexion between passivity and the photoelectric sensitiveness of metals has been examined (Allen, A., 1913, ii, 172). It is shown that the photoelectric sensitiveness of iron, zinc, and aluminium is greatly reduced after treatment with alcohol or water. In the case of copper, cobalt, nickel, silver, gold, and palladium, a similar treatment brings about only the slightest reduction of the photoelectric sensitiveness; in the case of platinum there is no change at all. All oxidising agents, which render iron, nickel, and cobalt passive, strongly reduce the photoelectric sensitiveness, whilst reducing agents, particularly nascent hydrogen, increase it. The above action is more intense the longer the reagents remain in contact with the metal. The same phenomenon is observed in the case of platinum and palladium, and also in metals which do not become passive, proving that the parallelism between passivity and photoelectric sensitiveness as found by Allen (*loc. cit.*) is incorrect. In the case of gold, silver, zinc, copper, and aluminium, the photoelectric sensitiveness is greatly reduced by oxidising agents and increased by reducing agents. The above results are explained as follows. The reduction of the photoelectric sensitiveness of iron, aluminium, and zinc by treatment with alcohol or water is attributed to the formation of a thin film of oxide. That no such action occurs in the case of the nobler metals is due to the greater difficulty experienced in oxidising these elements. The great increase in the photoelectric sensitiveness brought about by hydrogen points to the fact that hydrogen is the carrier of photoelectric sensitiveness. That all metals when charged with hydrogen become strongly photoelectric supports this view. J. F. S.

***X*-Ray Bulb with Liquid Mercury Anticathode and Wave-Length Measurements of the *L*-Spectrum of Mercury.** ALEX MÜLLER (*Phil. Mag.*, 1921, [vi], **42**, 419—427).—An arrangement is described in which an anticathode of liquid mercury is bombarded by cathode rays for the production of the *X*-ray spectrum. The wave-lengths of 14 lines in the *L*-spectrum are given, varying from 834·8—1418·3 ($\times 10^{-11}$ cm.). J. R. P.

Effect of the Rays from Radium, *X*-Rays, and Ultra-violet Rays on Glass. J. R. CLARKE (*J. Soc. Glass Technology*, 1921, **5**, 155—165).—A series of soda-lime glasses of the same composition, except that some contained selenium, some cobalt oxide, and others no admixture, have been exposed to the action of α-, β- and γ-rays, β- and γ-rays, γ-rays, *X*-rays, and ultra-violet rays respectively. All glasses containing selenium or cobalt oxide were coloured brown by β-rays, the depth of coloration corresponding with the range of the β-particles in the glasses. The intensity of coloration was greatest at the surface, decreased toward the interior, and increased with increasing selenium or cobalt oxide content. As the radiation was prolonged, the intensity increased to a maximum which depended on the percentage of colouring agent, and then remained constant. The pure soda-lime glass was only affected by α-rays,

being faintly coloured on the surface only. None of the glasses were affected by X-rays, γ-rays, or ultra-violet rays. All the glasses fluoresced in radium emanation, but a fatigue effect was observed at about the same time as the attainment of maximum intensity of coloration. The coloration of glasses is regarded as due to the formation of colloidal particles in the glass. The presence of such particles is explained as being due to the action of α- or β-rays on ions already present in the glasses. The fluorescence is held to be due to mechanical bombardment of the glass molecules by the rays. J. F. S.

Soft Characteristic X-Rays from Arcs in Gases and Vapours. F. L. MOHLER and PAUL D. FOOTE (*J. Washington Acad. Sci.*, 1921, **11**, 273—274).—If an electron current is maintained by a potential V between a hot cathode and anode in a vapour at low pressure, successive changes in the spectrum excited by electron impact occur, as V is increased. The maximum frequency of each additional group of lines, ν, is related to the minimum exciting potential by the quantum equation $Ve=h\nu$. The stages in the discharge were studied by measuring the photoelectric effect of the radiation on two other electrodes entirely shielded from ions produced in the arc. The photoelectric current plotted as a function of the exciting voltage shows nearly a linear relation with changes of slope at critical potentials. In this way potentials are found which are determined by the limiting frequency of the softest X-ray series of sodium, magnesium, phosphorus, sulphur, chlorine, carbon, nitrogen, and potassium. A new X-ray series of feeble intensity was detected. J. R. P.

Nickel Isotopes. F. H. LORING (*Chem. News*, 1921, **123**, 81).—Certain modifications in previous calculations (see A., 1920, ii, 171) are made in view of the announcement of the existence of isotopes of nickel, of atomic weights 58 and 60, by Aston (*Nature*, 1921, **108**, 520). J. R. P.

Variation of Resistance of Selenium with Temperature. SNEHAMOY DATTA (*Phil. Mag.*, [vi], **42**, 463—470).—The change of resistance of selenium with temperature is given by the equation $R_t=[65{\cdot}01+0{\cdot}86t+0{\cdot}0029t^2]\times10^5$ ohms. The constants depend on annealing and on the past history of the cell. Not more than 0·04 of the " light effect " is attributable to the heat produced by light. A change of colour accompanies the change in resistance on warming crystals of selenium produced by sublimation. The experiments suggest that if transformation into allotropic forms occurs, as seems probable, this takes place at all temperatures and the various modifications are in dynamic equilibrium, the quantity of each variety depending on the temperature. The degree of stability of each modification depends on the time during which it is maintained at one temperature. J. R. P.

Chemical Action of the Electric Discharge. I. G. POMA (*Gazzetta*, 1921, **51**, ii, 58—70).—A critical résumé is given of the different views which have been expressed regarding the nature of

the mechanism of the chemical actions exerted by the electric discharge (cf. following abstracts). T. H. P.

Chemical Action of the Electric Discharge. II. G. Poma and G. Bassi (*Gazzetta*, 1921, **51**, ii, 71—79).—The vapours of a number of organic compounds have been subjected to the action of an intense explosive discharge from an induction coil, the resulting mixture of products being analysed. Compounds of low molecular weight lead to no separation of carbon, this commencing with compounds containing four atoms of carbon in the molecule and increasing with more complex compounds. Compounds with several oxygen atoms in the molecule form, in addition to carbon, water and various organic compounds, the latter in proportions too small to admit of analysis.

Methyl alcohol decomposes almost completely in accordance with the equation $CH_3{\cdot}OH = CO + 2H_2$, only small proportions of carbon dioxide, acetylene, and methane being formed. With the higher alcohols, however, considerable quantities of acetylene and methane are obtained; the proportions of acetylene and carbon monoxide appear to depend solely on the molecular weight of the alcohol, whereas those of methane and hydrogen are influenced also by the molecular structure, the methane increasing with the proportion of methyl groups in the molecule.

Formic acid vapour gives approximately 1, 2, and 1 vols. of carbon dioxide, carbon monoxide, and hydrogen respectively, together with small amounts of acetylene and methane; the decomposition evidently occurs in two ways, represented by the equations, $H{\cdot}CO_2H = CO_2 + H_2$ and $2H{\cdot}CO_2H = 2CO + 2H_2O$. When, however, the molecular weight is increased, either by esterification of the formic acid or by passage to higher homologues, the proportion of carbon dioxide formed diminishes considerably, but not regularly. T. H. P.

Chemical Action of the Electric Discharge. III. G. Poma and A. Nesti (*Gazzetta*, 1921, **51**, ii, 80—94).—By means of a Siemens ozoniser the action of the dark electric discharge on the vapours of a number of compounds has been investigated. With methyl alcohol, the mixture of gaseous products formed has the following percentage composition by volume: carbon monoxide, 10·8; methane, 15·5, and hydrogen, 73·3; formaldehyde is produced, but the other liquid and solid products of the reaction have not yet been investigated. The changes taking place are probably represented by the equations: $CH_3{\cdot}OH = CO + 2H_2$, $2CH_3{\cdot}OH = 2CH_4 + O_2$, and $CH_3{\cdot}OH = H{\cdot}CHO + H_2$; the oxygen liberated probably unites with hydrogen to form water.

With ethyl alcohol, the gaseous products contain, in percentages: carbon dioxide, 2·2; carbon monoxide, 4·4; acetylene and ethylene, 9·0; methane and ethane, 26·0, and hydrogen, 59·0; acetaldehyde and other products are also formed. In the case of formic acid, the decomposition appears to take place according to the two equations, $H{\cdot}CO_2H = CO_2 + H_2$ and $2H{\cdot}CO_2H = 2CO + 2H_2O$, the gaseous products containing 22·4% of carbon dioxide, 53·6% of

carbon monoxide, and 23·8% of hydrogen; the liquid product distils completely. With acetic acid, the gaseous products have the percentage composition: carbon dioxide, 35·4; carbon monoxide, 18·5; methane and ethane, 17·3, and hydrogen, 28·3, and are apparently formed by the reactions, $2CH_3 \cdot CO_2H = 2CO_2 + C_2H_6 + H_2$ and $CH_3 \cdot CO_2H = CH_4 + CO_2$; the liquid product distils without residue. In the case of acetone vapour, the electrical conductivity is greater than with the above compounds, and less gaseous products are formed, the percentage composition of these being: carbon dioxide, 1·6; acetylene and ethylene, 5·0; carbon monoxide, 38·1, and methane and ethane, 55·3; hence for the gaseous phase the principal reaction is $CH_3 \cdot CO \cdot CH_3 = CO + C_2H_6$. The liquid products contain a γ-diketone, probably acetonylacetone. With methyl ethyl ketone vapour, the gaseous products have the percentage composition: acetylene and ethylene, 12·5; carbon monoxide, 32·8; methane and ethane, 43·6, and hydrogen, 10·2; the liquid products were shown to contain *s*-dimethylacetonylacetone, but were not analysed completely.

In general, the dark electric discharge favours endothermic chemical reactions, although in some cases it may determine the sudden rupture of a false equilibrium, and hence cause an exothermic reaction. To a certain point parallelism exists between the action of the dark electric discharge and that produced by a rapid rise in temperature, although such parallelism is evidently imperfect. T. H. P.

Anodic Behaviour of Metals in Non-aqueous Solutions. II. Behaviour of Various Metals in Acetone Solutions. UMBERTO SBORGI and PAOLO MARCHETTI (*Nuovo Cim.*, 1921, [vi], **22**, 151—175).—The authors have investigated the anodic behaviour of various metals in acetone solutions of lithium chloride and silver nitrate, the apparatus and methods employed being identical with those used in the experiments on methyl alcoholic solutions (*Atti R. Inst. Veneto*, July, 1921).

In saturated solution of lithium chloride in acetone, anodes of nickel, cobalt, iron, zinc, and cadmium dissolve as bivalent metals and copper as a univalent metal, whilst aluminium dissolves to an extent greater than that calculated for a tervalent metal. The various phenomena accompanying the attack of the metal, such as formation of precipitates, coloration of the anodic liquid, etc., are discussed for each case. At the platinum cathode there takes place evolution of gas, deposition of lithium and lithio-acetone, and formation of precipitates containing the anode metal.

In saturated solutions of silver nitrate in acetone, anodes of iron, nickel, and cobalt exhibit passivity under various conditions and those of lead and aluminium show partial mechanical passivity, whilst copper is dissolved as a bivalent metal; the passifying influence of acetone is evident in all these cases.

These results and those obtained with nickel anodes in methyl alcoholic solutions (*loc. cit.*) show that metals that are passive and anions which are passifying in aqueous solutions exhibit the same

characteristics in non-aqueous solutions, although the solvent itself also exerts a decided influence. T. H. P.

Hydration of the Lithium Cation. J. BARBOROVSKÝ and V. HANÁK (*Chem-Listy*, 1921, **15**, 3—5).—The authors determined by a direct gravimetric method the increase in weight of the solution of lithium chloride at the cathode. The amounts of lithium chloride and water that were carried to the cathode were calculated from the difference between the initial and final concentrations of the cathode solution. These data yielded the transport number of the lithium ion and the amount of water associated with the lithium ion. Presupposing that the chloride ion has no affinity for water, it is indicated that eighteen molecular proportions of water are linked with the lithium ion. CHEMICAL ABSTRACTS.

Application of the Law of Mass Action to Strong Electrolytes and the Derivation of the General Equation of the Ionisation Isotherm. WILLIAM HUGHES (*Phil. Mag.*, 1921, [vi], **42**, 428—431).—The equation previously deduced (this vol., ii, 481) is applied to obtain a general relation between V and α, of which the equations of Ostwald, Rudolphi, van't Hoff, and Partington are special cases. Complete ionisation need not be assumed, and the law of mass action holds good in the case of strong electrolytes if active mass is represented by a momentum term, as is necessary in all applications of the law. The suggestion that the abnormality of strong electrolytes is due to the abnormal osmotic behaviour of the ions is in entire agreement with the fundamental assumptions made. J. R. P.

The Transformation of Iron at the Curie Point. P. DEJEAN (*Compt. rend.*, 1921, **173**, 412—414).—A comparison of the intensity of magnetisation of a cylindrical steel bar 1·2 m. long and 20 mm. in diameter with that of a similar bar composed of 120 small cylinders 10 mm. long and 20 mm. in diameter having varying definite interspaces between the small cylinders. The variation of the intensity of magnetisation with the interspace is of the same type as its variation with temperature. This is explicable if an increase in temperature provokes a progressive spreading of the elementary magnets in the bar. This may be produced by a progressive transformation of a magnetic α-form, stable in the cold, into an isomorphous, non-magnetic β-form, stable at higher temperatures or simply by a spreading of the magnetic elements progressive with rise in temperature. W. G.

The Importance of Experiments at Very Low Temperatures. C. A. CROMMELIN (*Chem. Weekblad*, 1921, **18**, 483—487, 499—503, 515—519).—A discussion chiefly of the work of Kamerlingh Onnes and his co-workers at Leiden on critical point phenomena, and the relation between magnetic susceptibility and temperature. S. I. L.

Relationships of the van der Waals Constants. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 373—375).—A theoretical paper in

which it is shown that van der Waals's constants, a and b, in the case of non-associated liquids, can be calculated from: the number of atoms in the molecule (n), the number of valencies in the molecule (z), from critical data, and other constants. In the case of the constant b, the value may be ascertained by the expressions (1) $b=412n10^{-6}$; (2) $b=201z10^{-6}$; (3) $b=795{\cdot}16M^{2}10^{-4}/T_s^{2}d_s$; (4) $b=12354d_s10^{-3}/p_k^{2}$. The value of b as calculated by each of these expressions is recorded for twelve substances and the results are compared with the standard values. It is shown that there is an approximate agreement among the values, those obtained from formula 4 being the least in agreement. The constant a calculated from, (5) $a=5{\cdot}094nT_k10^{-6}$; (6) $a=2{\cdot}49z{\cdot}T_k10^{-6}$; (7) $a=4{\cdot}5846n^{2}p_k10^{-6}$; (8) $a=1474{\cdot}713M^{2}10^{-6}/T_sd_s$ and (9) $a=239920d_sT_s10^{-6}/p_k^{2}$. The value of a is calculated by all the above formula for eleven substances, and a fair general agreement with the accepted values obtained. A formula is developed whereby the coefficient of expansion of normal organic liquids may be calculated from the van der Waals constants. This has the form $K_{20}=1\{(a/0{\cdot}006186)-293\}$. The agreement between the value of K_{20} calculated by the above formula and the experimental value is moderate. J. F. S.

Nernst's Heat Theorem and Chemical Constant. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1920, **41**, 19—35).—A mathematical paper, in which the explanations of the constant by Nernst and by Sackur are criticised. Calculated values, in good agreement with Nernst's values, are given for a number of substances.
CHEMICAL ABSTRACTS.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. IV. The Constituents of Anthracene Oils. PAUL PASCAL (*Bull. Soc. chim.*, 1921, (iv), **29**, 644—656; cf. A., 1913, ii, 292, 304, 1031).—The author has determined the melting-point curves of binary mixtures and some ternary mixtures of anthracene, phenanthrene, acridine, carbazole, retene, chrysene, and 4-methylacridine. Anthracene, phenanthrene, and carbazole, taken two by two or all three together, give a continuous series of mixed crystals. The melting-point curves of binary mixtures containing acridine as one component always show a minimum point. The introduction into a binary mixture of a constituent with an unsymmetrical molecule almost always results in isodimorphism, except in some cases when the lack of symmetry is due simply to the structure of side chains substituted in two symmetrical nuclei. W. G.

Standardised Method for the Determination of Solidification Points, especially of Naphthalene and Paraffin. R. M. WILHELM and J. L. FINKELSTEIN (*Bur. Standards, Sci. Papers*, 1919, **340**, 158—197).—The apparatus consists of a test-tube with thermometer and glass stirrer air-jacketed by insertion through the cork of a wide-mouthed bottle, which is immersed in a water-bath. The solidifying point corresponds with the first series of five or more readings, during which the temperature remains constant

($\pm 0{\cdot}02°$). Usually under-cooling will occur, in which case the constant temperature should be observed immediately after the under-cooling ceases. CHEMICAL ABSTRACTS.

The Efficiency of certain Fractionating Columns in Distillation in a Vacuum. Some Laboratory Designs. L. SMITH (*J. pr. Chem.*, 1921, **102**, 295—304).—A preliminary account is given of the use of a large number of fractionating columns in the distillation of a mixture of glycerol monochlorohydrins under diminished pressure. The viscosity of the mixture inhibits the employment of all those types in which heads are used. It is found that the bulbous columns (including the Young " evaporator " still-head) have in general little efficiency and are markedly inferior to the " rod and disk " and Vigreux types. The reason of this is to be found in the incomplete mixing of the vapours in the more voluminous apparatus, a defect which must be more apparent in vacuum than in ordinary distillation, on account of the much greater velocity of the stream of vapour. The rate of distillation has an unexpectedly great effect on the separation; an efficient Vigreux column did not give any better result than the worst head when the rate of distillation with the former was two and a half times as great as with the latter. Efficient separation can only be obtained by distilling as slowly as possible, but, under these conditions, it is exceedingly difficult to keep the process uniform. H. W.

The Arrangement of the Molecular Volumes of the Oxides in the Periodic System. D. BALAREFF (*J. pr. Chem.*, 1921, **102**, 283—286).—A new table of molecular volumes of solid oxides is given. The graph showing the connexion between this factor and the atomic weights of the elements does not exhibit any striking regularity. The curves of the individual sub-groups are more uniform, eight of them having a minimum in the first portion. H. W.

Influence of Temperature on the Viscosity of Normal Liquids. EDM. VAN AUBEL (*Compt. rend.*, 1921, **173**, 384—387).—The variation of the viscosity of normal liquids with temperature may be represented by the equation $\phi=m+n \log (\theta-t)$, where ϕ is the inverse of the viscosity, t is the temperature observed, θ is the critical temperature of the liquid, and m and n are constants. This equation is verified in the cases of chlorobenzene, ethyl acetate, and benzene. W. G.

The Dimensions of the Molecules of Fatty Oils and some Phenomena of Molecular Solutions. PAUL WOOG (*Compt. rend.*, 1921, **173**, 387—390; cf. *ibid.*, 1921, **173**, 303).—If a solid saturated fat and an unsaturated liquid fat in separate benzene solutions are poured successively on to water the products cover a surface equivalent to the sum of the areas of the molecules considered separately. They orientate freely on the water and do not influence one another. If, however, the two fats are dissolved together in benzene and the solution is poured on to water, the area covered

by the mixed molecules differs from the area calculated by addition. This phenomenon is attributed to an influence of the unsaturated molecules on the solid molecules. W. G.

Behaviour of Cotton and Wool toward Substantive Dyes. R. HALLER (*Kolloid Zeitsch.*, 1921, **29**, 95—100).—It has been shown that diamine-blue-3R dyes vegetable fibre, as instanced by cotton, blue, whilst animal fibre is dyed corinth-red, as shown by wool. The behaviour of this dye has been investigated. It is shown that, as in the case of congo-rubin (this vol., ii, 28) solutions of diamine-blue-3R consist of particles of different degrees of dispersion. The highly disperse particles are corinth-red in colour, whilst the less dispersed particles are blue. These two types of particles may be readily separated by ultra-filtration. It is pointed out that generally cotton is dyed by the larger particles and wool by the more dispersed particles. This point is considered in connexion with the acid dyes and the benzidine dyes; the former are very highly dispersed whilst the latter consist of much larger particles, and it is the former class which dyes wool. It is pointed out that for each type of fibre (animal or vegetable) there is a definite specific degree of dispersion of the dye necessary for the maximum colour effect. In the cases of congo-rubin (*loc. cit.*) and diamine-blue-3R it has been shown that the degree of dispersion may be changed by the addition of neutral salts; hence it follows that by the use of a suitable concentration of a given neutral salt every substantive cotton dye is capable of becoming a usable wool dye. J. F. S.

The Determination of Surface Tension from the Rise in Capillary Tubes. SAMUEL SUGDEN (T., 1921, **119**, 1483—1492).

Application of Dalton's Law to Concentrated Solutions. RADU CERNATESCO (*Ann. sci. Univ. Jassy*, 1920, **10**, 259—292; from *Chem. Zentr.*, 1921, iii, 199).—The freezing-point depressions of pairs of non-electrolytes were determined separately and when mixed for the same solvent. The osmotic pressure of the mixture may be less or greater than the sum of the osmotic partial pressures. The relation of the osmotic pressure to the sum of the partial pressures may also be reversed with increase or decrease of concentration. The Abegg formula is inadequate, and the facts can only be explained with the help of van der Waals's theory. A new formula for the osmotic pressure of mixtures, based on the modified Nernst formula of Bogdan (*Chem. Zentr.*, 1916, i, 1006) is devised. The anomalies observed in freezing-point depressions with strong electrolytes are probably due also to the fact that observed depressions are not equal to the separate partial depressions. G. W. R.

Formation and Stability of Modifications of Polymorphous Substances Below their Transition Temperature. O. MÜGGE (*Centr. Min.*, 1921, 504—505).—In reply to Brauns's criticism of the author's explanation of the genesis of doubly refracting boracite (this vol., ii, 387), it is pointed out that in the case of this mineral the transition from the highly symmetrical to the mimetic modi-

fication takes place with such rapidity that it is unlikely that growth could ever take place in the former modification at a low temperature. A temperature of 265° is assumed to have occurred only locally as a result of chemical processes. E. H. R.

Low Concentrations in Colloid Chemistry. H. R. KRUYT (*Chem. Weekblad*, 1921, **18**, 475—479).—A paper recapitulating the present knowledge of the influence of traces of electrolytes on the stability of colloidal sols. S. I. L.

Sulphide Sols. II. Sol Preparation by means of Gaseous Hydrogen Sulphide. FRIEDRICH-VINCENZ VON HAHN (*Kolloid Zeitsch.*, 1921, **29**, 139—143).—The author has investigated the production of metallic sulphide sols by the action of gaseous hydrogen sulphide on solutions of salts. The influence of temperature, rate of passage of the gas, and duration of the treatment on the stability of the resulting sol has been particularly considered. These three factors are shown to have a determining influence on the stability. The velocity of precipitation is known to have a considerable influence on the dispersion of the resulting system. The more rapid the formation the greater in general is the degree of dispersion. In the present case, the formation of the precipitate reaches its maximum velocity when the duration of treatment with the gas has reached a definite value; consequently further treatment is without any influence on the stability of the system. The same applies to the temperature; that is, there is a particular temperature at which the velocity of precipitation, the dispersion, and the stability of the sol produced are at a maximum and further increase of temperature is without influence. The velocity of precipitation increases also with the rate of passage of the gas. All three factors tend to increase the velocity of formation and thereby the degree of dispersion, which means an increase in the stability (cf. this vol., ii, 40). J. F. S.

Theory of Gels. III. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1921, **15**, 553—562; cf. A., 1920, i, 452).—The reversible sol-gel transformation of the natural emulsoids is an extreme case of crystallisation and solution in conformity with von Weimarn's ideas. The true solubility of gelatin in water at 18° is 0·12 gram per 100 c.c. A 0·13% solution is metastable and has a blue opalescence. On slight increase of concentration, the gelatin is deposited as particles, mostly just below microscopic size. A further increase of concentration increases the bulk of the precipitate, the particles decrease in size, and at about 0·7% the precipitate fills the solution as a white, cloudy jelly. Similar results were obtained with agar, and small sphærites with starch. Clear gelatin gels become opalescent and develop sphærites on prolonged keeping. G. B.

General Colloidal Chemistry. II. Time Change of Colloidal Stannic Acid after Peptisation with Alkali Hydroxide Solution. ADOLF STIEGLER (*Kolloid Zeitsch.*, 1921, **29**, 65—81).—The electrical conductivity and hydrogen-ion concentration of solutions of

stannic acid in potassium hydroxide of varying concentrations have been determined at 25° at various times over long periods. It is shown that colloidal stannic acid after peptisation with potassium hydroxide shows a change in its specific conductivity with time. With a series of solutions of stannic acid of different amounts of stannic acid in a solution of potassium hydroxide of constant composition, it is found that the solutions richer in tin undergo an immediate increase in specific conductivity, whilst the solutions poorer in tin at first suffer a decrease in conductivity followed by an increase. The increase in conductivity continues for months at a steadily decreasing rate. The concentration of hydroxyl ions decreases with time and is complete in about eight days. The specific conductivity of the colloidal portion has, in hydroxide solutions of all concentrations, a final value for the conductivity which is two to three times the initial value. The cause of the change in conductivity is considered, and shown not to be due to "temporary hydrolysis," as has been previously thought. The reactions represented by the equations (*a*) $AB+HOH \rightleftarrows AH+BOH$; $mBOH+nAB \rightleftarrows mBOHnAB$; (*b*) $AB+HOH \rightleftarrows AH+BOH$; $2BOH \rightarrow B_2O+H_2O$, may be taken as representing the cause of the conductivity changes. J. F. S.

The Hydration of the Fibres of Soap Curd. I. The Degree of Hydration determined in Experiments on Sorption and Salting Out. JAMES WILLIAM MCBAIN and HERBERT ERNEST MARTIN (T., 1921, **119**, 1369—1374).

The Hydration of the Fibres of Soap Curd. II. The Dew-point Method. JAMES WILLIAM MCBAIN and CYRIL SEBASTIAN SALMON (T., 1921, **119**, 1374—1383).

Structures in Disperse Systems. G. WEISSENBERGER (*Kolloid Zeitsch.*, 1921, **29**, 113—124).—A theoretical paper in which the structure of disperse systems is considered on the basis of a large amount of work published by the author and others. It is shown that solutions of dispersoids, when a definite concentration is exceeded, possess a tendency whereby the particles assume an ordered arrangement. The cause of this is found in the interference with the free spatial movement of the particles. Consequently, the phenomenon is not observed in suspensoids, since these have particles which, not being surrounded by a water sheath, are very small and their free movement is not interfered with until the concentration becomes very great. On the other hand, emulsoids and pseudo-emulsoids, which have particles surrounded by water sheaths and consequently may be very large, are systems in which the hindrance to free motion may be very great and is readily observed. Even at low concentrations, this occurs and furnishes the tendency to the structure formation. The elements of structure formation are the primary particles (micellæ); these may be either of a crystalline nature or a conglomeration of molecules. The arrangement of the molecules in these aggregates follows definite laws, since in similar circumstances

the same aggregates are always produced, but a change in the conditions brings about a change in the size and density of the aggregate. The primary particles are resistant and are the carriers of chemical reactions; they may preserve their size and other properties unchanged through a chemical reaction. In emulsoids and dispersoids, small discontinuities are often observed microscopically. These are not accidental, since the same type of discontinuity always occurs in identical circumstances. In addition to the primary structure elements, larger structure elements are also formed by the aggregation of numbers of primary elements. In such structure aggregates, the area of the particles actually touching becomes smaller in relation to the total mass the larger the number of primary structure elements composing the aggregate, and in consequence the solidity and resistance of the structure decreases very rapidly the larger the secondary structure elements. These colloidal structures are destroyed by chemical and mechanical forces in exactly the same way as crystalline structures, and are reformed in the same way. There is a concentration region where the formation of a colloidal structure is at its optimum, which is generally found in the region of small dispersion and in the neighbourhood of the turbidity conditions. By suitably choosing the concentration relationships, it is possible to follow the formation of the colloidal structure microscopically right up to the macroscopic structure. J. F. S.

Colloid-Chemical Phenomena in the Tyrosinase Reaction. HUGO HAEHN (*Kolloid Zeitsch.*, 1921, **29**, 125—130; cf. this vol., ii, 528).—The author has investigated the nature of the variously coloured melanin obtained in the tyrosinase reaction. In the ordinary course of the reaction, the melanin passes through a series of colours, red, brown, violet, blue, and black. It is shown that the ferment tyrosinase consists of two parts, the enzyme, α-tyrosinase, and an inorganic salt. Neither the enzyme nor the inorganic salt alone will effect the reaction, but a mixture of the enzyme and an inorganic salt (calcium chloride, zinc sulphate, cadmium sulphate, and many others) effects the reaction, although not always is the scheme of colours passed through, but the black product is obtained in every case. A number of experiments tend to show that the essential difference between the red and black melanin is a difference in the degree of dispersion. This cannot be definitely proved until the constitution of melanin is established, but both substances undergo similar changes, for example, with hydrosulphite, and are thus shown at least to be similar. Both substances are negatively charged. The tyrosinase reaction is shown to be composed of two parts, (*a*) a biochemical, and (*b*) a colloid-chemical reaction. In the former, the α-tyrosinase breaks up the tyrosine molecule and in the presence of the inorganic salt builds up the red melanin molecule. This is followed by the second reaction, in which coagulation changes the finely disperse red phase into the coarsely disperse black phase, after which precipitation occurs. J. F. S.

New Physico-chemical Law. The Law of Variability. JOSEPH ERLICH (*Ann. Chim. Analyt.*, 1921, **3**, 246—250).—A theoretical paper in which the variability of a system is discussed. It is shown that it is often not simple to fix the variability from considerations of the phase rule, this involving as it does the arbitrary quantity, "number of components." The present paper gives a method of fixing the variability of a system in all cases where the concentrations are only susceptible of change in relation to one and the same phase, the rest remaining invariable. It is shown that where gases constitute one of the phases of a system, the variability is equal to the number of gases, and in systems in solution where there is no gaseous phase, the variability is equal to the number of substances less one. J. F. S.

Physico-chemical Study of the Double Decomposition, $(NH_4)_2B_4O_7+2NaCl \rightleftarrows Na_2B_4O_7+2NH_4Cl$, for the Technical Preparation of Borax. U. SBORGI and C. FRANCO (*Gazzetta*, 1921, **51**, ii, 1—57).—The authors first discuss the theoretical considerations relating to systems containing reciprocal pairs of salts in solution and the methods of representing graphically their solubilities in water. The system corresponding with the equation $(NH_4)_2B_4O_7+2NaCl \rightleftarrows Na_2B_4O_7+2NH_4Cl$ has been investigated at 0°, 10°, and 25°, it being found that the pair stable in a temperature zone below 25° is the one containing borax; the data obtained are expressed in accordance with Jänecke's formula. The solubility diagrams exhibit two invariant points, at constant pressure and constant temperature, the solid phase consisting of (I) $NaCl+Na_2B_4O_7,10H_2O+NH_4Cl$, or (II) $(NH_4)_2B_4O_7,4H_2O+Na_2B_4O_7,10H_2O+NH_4Cl$; with the first there corresponds a congruent, and with the second an incongruent solution, the so-called transformation interval lying in the temperature zone considered.

The yield of borax is calculated for each point of the solubility diagram, the highest yields corresponding with that portion of the curve joining points (I) and (II) (above) nearest to the latter. T. H. P.

Deduction of the Laws of Chemical Statics from the Theorem of Virtual Work. R. ARIANO (*Gazzetta*, 1921, **51**, ii, 95—108).—In this mathematical paper it is shown to be possible to enunciate, as a single principle, the theorem of virtual work, which serves as the starting-point for the exact treatment of all problems of equilibrium. The co-ordination of chemical and mechanical statics thus produced aids in the deduction, from the comparison between various phenomena, of the general laws governing a large number of natural phenomena. Various applications of the principle are developed. T. H. P.

Reaction in the Dark between Chlorine and Trichlorobromomethane. ALEXANDRA VON RANKE (*Zeitsch. Elektrochem.*, 1921, **27**, 365—367.; cf. Noddack, this vol., ii, 568).—The reaction between chlorine and trichlorobromomethane has been examined at 100°. The reacting substances were sealed in bulbs in such a way

that the chlorine was entirely dissolved and no gas space left. Other experiments were carried out in which the chlorobromomethane was diluted with 3—255 volumes of carbon tetrachloride. The reactions were allowed to proceed until a definite brown tint was reached, when the amount of bromine set free was estimated spectrophotometrically. The velocity of the bromine separation decreases with the dilution. From this it follows that the primary reaction is not due to the chlorine atoms. The velocity constant for the reaction is given by the equation $K_2=[Br_2]/[Cl_2].[CCl_3Br].t$, from which the course of the reaction is regarded as follows: (i) $Cl_2+CCl_3Br=CCl_4+Cl+Br$, (ii) $Cl+CCl_3Br=CCl_4+Br$, (iii) $Br+Br=Br_2$. J. F. S.

The Rate of Hydrolysis of Ethyl Orthoformate. ANTON SKRABAL and OTTO RINGER (*Monatsh.*, 1921, **42**, 9—46).—The hydrolysis of ethyl orthoformate takes place in accordance with the two separable equations: $CH(OEt)_3+H_2O \longrightarrow H{\cdot}CO_2Et+2EtOH$ and $H{\cdot}CO_2Et+H_2O \longrightarrow H{\cdot}CO_2H+EtOH$. The second reaction is the ordinary ester hydrolysis; its already determined velocities in an acid and alkaline medium have been measured again, and the values $k_s=0{\cdot}192$ and $k_a=1080$ at 25° are confirmed. The first reaction is shown to proceed too slowly in alkaline solution to permit measurement, so that ethyl orthoformate is not noticeably hydrolysed by water alone or under the influence of hydroxyl ions. On the other hand, in strongly acid solution it proceeds with extreme rapidity. The formation of formic acid from the ortho-ester in solutions of mineral acids must therefore occur at a rate equal to that of the acid hydrolysis of ethyl formate; this is shown to be the case. The rapid reaction can be measured in the presence of a hydrogen buffer solution of primary and secondary phosphate, the course of the change being followed by measurement of the ethyl formate present after known intervals of time. The latter is only very slightly attacked under the experimental conditions adopted. It is thus possible to isolate the process of hydrolysis of ortho-ester to formic ester and to measure its rate in a medium of constant acidity. The results show that it is a reaction of the first order and that a proportionality exists between the velocity and the hydrogen-ion concentration. On the basis $[H^{\cdot}]=1$, the velocity constant $k=70{,}000$, which is unusually high in comparison with other acid hydrolysis constants.

In connexion with his experimental results and the similar investigations of Verkade (A., 1914, ii, 256; 1916, ii, 234, 607; 1918, ii, 103), the hydrolysis of the three types, ROR′, AOR, AOA′ (in which R=alkyl, A=acyl), is discussed and it is shown that ethyl orthoformate belongs to the ether type. H. W.

Hydrolysis of Ethyl Oxamate. ANTON SKRABAL and GRETE MUHRY (*Monatsh.*, 1921, **42**, 47—62).—The methods used are similar to those adopted with oxalic esters (A., 1917, ii, 250; 1919, ii, 144). The hydrolysis in alkaline solution is effected in the presence of disodium phosphate: $CO_2R{\cdot}CO{\cdot}NH_2+Na_2HPO_4+H_2O=CO_2Na{\cdot}CO{\cdot}NH_2+NaH_2PO_4+R{\cdot}OH$. The course of the change is

followed by titration of the unaffected disodium to monosodium phosphate by $N/10$-hydrochloric acid in the presence of methyl-orange. The velocity constant for $[OH']=1$ at 25° is found to be 48,000 for the methyl and 22,000 for the ethyl ester. The hydrolysis is also measured in $N/10$-hydrochloric acid solution, and is followed by titration with $N/10$-ammonia solution in the presence of alizarine; for $[H^{\cdot}]=1$, the velocity constants are calculated to be 0·0020 and 0·0015 for the methyl and ethyl esters respectively.

The communication concludes with a long theoretical discussion, based on the results obtained by the author with oxalic esters, of the influence of change in one group on the reactivity of the second group in the case of symmetrical di-esters. It is frequently observed that such alterations which do not affect the second group with regard to one particular type of action are also without influence in all other kinds of action. H. W.

Catalytic Actions at Solid Surfaces. VI. Surface Area and Specific Nature of a Catalyst: Two Independent Factors controlling the Resultant Activity. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1921, [*A*], **99**, 490—495; cf. A., 1920, ii, 608).—The apparent volume of reduced nickel prepared in various circumstances has been determined and compared with the catalytic activity of the preparation. It is shown that nickel hydroxide reduced on kieselguhr gives a much larger volume than the same substance or the fused oxide reduced in the absence of kieselguhr, and that this product is very much more active than the nickel produced from the other sources. The rate of reduction of nickel oxide is also studied. The time–reduction curves show an inflexion point which depends on the physical state of the oxide and the temperature. The authors consider that the more rapid initial reduction represents the production of metallic nickel from the surface of the oxide particles, the slower subsequent rate corresponding with the reduction of a denser central core of oxide: such partly reduced oxide represents a supported catalyst as in the case of reduced nickel on kieselguhr, and its superior activity is to be attributed to the same cause as that of the kieselguhr-nickel oxide. The relation of the activity of a supported nickel catalyst to its reduced metal content has been ascertained in the case of the hydrogenation of cotton-seed oil at 180°. The results show that the variations in the catalytic power of reduced nickel are to be ascribed to the different surface areas of the free nickel exposed, and do not require for their interpretation the assumption of the presence of any catalyst (such as an oxide) other than metallic nickel. J. F. S.

The Stability of Atoms. (SIR) ERNEST RUTHERFORD (*Proc. Physical Soc.*, 1921, **33**, 389—394).—A lecture delivered before the Physical Society of London on June 10, 1921. A. A. E.

Constitution and Stability of Atom Nuclei. WILLIAM D. HARKINS (*Phil. Mag.*, 1921, [vi], **42**, 305—339).—Seven experimental correlations between the stability and composition of atomic nuclei are summarised. Three methods of classifying

isotopes are: (1) into four classes according as the number of electrons and protons in the nucleus is odd or even; (2) into isotopic numbers, varying from -1 for hydrogen and the lower isotope of helium, 0 for the most abundant atomic species, up to 54 for uranium; (3) according to series relationships. The problem of nuclear stability in relation to the above is discussed. There is a marked periodicity in the variation of abundance, atomic stability, and a number of functions which express the composition of atomic nuclei. The most important relations which can be utilised in the prediction of isotopes are that the ratio of electrons to protons in the nucleus is never less than 0·5 for stable atoms, and the number of isotopes is in general considerably greater for elements of even than for elements of odd atomic number. J. R. P.

Atomic Dimensions. MARIANO PIERUCCI (*Nuovo Cim.*, 1921, [vi], **22**, 189—198).—The author considers the question whether the numbers calculated by Bragg (A., 1920, ii, 538) as the true radii of the atoms are multiples of one and the same length, which he terms the " elementary length " (A., 1920, ii, 300). Division of the atomic volume by the Avogadro number gives what may be termed briefly the " volume of the atom," and from this, together with the assumption that the atom is spherical and that at the absolute zero the packing is as close as possible, the value of the " elementary length " is calculated to lie between 0·036 and 0·039 Å. The available data are insufficient to decide the above question, but from the table given by Bragg (*loc. cit.*) it is evident that the calculated atomic radii group themselves round the atomic radii of the inert gases, and that the atomic radii for neon, argon, krypton, and xenon are related almost exactly as the numbers, $4\Delta : 6\Delta : 7\Delta : 8\Delta$, Δ having the value 0·34 Å.; the latter is almost exactly nine times the " elementary length."

For the four inert gases for which Bragg has calculated the atomic diameter, D_A (*loc. cit.*), the latter (in Å.) is related to the absolute melting point, T_f, in accordance with the simple expression, $T_f = 79D_A - 81$. Bragg does not give the value of the atomic diameter of helium, but taking its absolute melting point as 0—2° Abs., the expression just given leads to the value 1·025—1·05 Å. for such atomic diameter. Since $3\Delta = 1{\cdot}01$ Å., the conclusion seems justified that the atomic radii of helium, neon, argon, krypton, and xenon are related as 3 : 4 : 6 : 7 : 8. T. H. P.

The Elements regarded as Compounds of the First Order. S. H. C. BRIGGS (*Phil. Mag.*, 1921, [vi], **42**, 448—456).—If the elements are regarded as compounds of the atomic kernels (that is, the residues when all the electrons in the outer shell are removed) and electrons, their reactions with each other are precisely analogous to the reactions between binary compounds; for example, (*a*) $K^kE + Cl^kE_7 = K^k[Cl^kE_8]$ (where E=electron) and (*b*) $2KCl + PtCl_4 = K_2[PtCl_6]$. There is no essential difference between the forces holding together atoms in a compound and those holding the kernels and electrons in an atom. There are only two elements, *proton*

and *electron*. The atomic kernels are compound radicles of proton and electron, some of which combine with electron to give strongly polar substances like alkali metals and others non-polar substances such as neon (cf. $NH_4+Cl=NH_4Cl$ and $C_6H_5+Cl=C_6H_5Cl$). The chemical elements are true compounds of the first order, Werner's "compounds of the first order" are really of the second order, and substances such as potassium platinichloride of the third order. Co-ordination is involved in all valency phenomena. J. R. P.

Encounters between Non-spherical Gaseous Molecules. A. O. RANKINE (*Proc. Physical Soc.*, 1921, **33**, 362—376).—An extension of the author's previous work (this vol., ii, 489) on molecular dimensions and structure derived from the combined data of the kinetic theory of gases and of *X*-ray crystal measurements. In the present paper, non-spherical molecules built up of atoms of unequal sizes are considered; the paper considers all cases of diatomic molecules and special cases of polyatomic molecules.

J. F. S.

Valency Theory of G. Lewis and the Asymmetry of the Water Molecule. EUSTACE J. CUY (*Zeitsch. Elektrochem.*, 1921, **27**, 371—373).—A theoretical paper in which, on the basis of the views put forward by Lewis (A., 1916, ii, 310) in connexion with the statical atom, the author has developed formulæ for the molecules of water, hydrogen sulphide, and ammonia. It is shown that in water the linking angle is approximately the same as that between carbon bonds. The distance between the oxygen nucleus and the hydrogen nuclei is the same in both cases, but is different from that between the two hydrogen nuclei. The well-defined dipolar character of water is expressed by the above, for two hydrogen atoms lie in one half of the tetrahedron and two electron pairs in the other half. The asymmetric nature of the water molecule is confirmed by the molecular heat, $6R/2$, whereas a symmetrical structure would demand $5R/2$. An asymmetric structure favours association more than a symmetrical structure. The cases of ammonia and hydrogen sulphide can be considered in the same way.

J. F. S.

Inorganic Chemistry.

Reversible Reactions of Hydrogen and Carbon Monoxide on the Metallic Oxides. GEORGES CHAUDRON (*Ann. chim.*, 1921, [ix], **16**, 221—281).—A more detailed account of work already published (cf. A., 1914, ii, 721; 1920, ii, 182, 379; this vol., ii, 178). W. G.

Iodine Monochloride. E. FOURNEAU and E. DONARD (*Bull. Sci. Pharmacol.*, 1920, **27**, 561—566).—The addition of sodium

chloride stabilises solutions of iodine monochloride to the same degree as does hydrogen chloride; it does not inhibit the first phase of iodine trichloride decomposition which yields iodine monochloride. A method for the estimation of iodine monochloride, based on the facts that, unlike free iodine, the monochloride is scarcely soluble in chloroform, whereas it is very soluble in ethyl ether, and that it liberates iodine from potassium iodide, yields results of moderate accuracy. CHEMICAL ABSTRACTS.

Density, Refractivity Relationship and Dispersion of Gaseous Nitrogen at its Boiling Point. ERICH GEROLD (*Ann. Physik*, 1921, [iv], **65**, 82—96).—The density of gaseous nitrogen at the boiling point has been determined by the displacement method. Six determinations are recorded at temperatures 77·68—77·77° Abs., and from the mean the value $d_g=0·0044973\pm17\times10^{-7}$ at 741·10 mm. and 77·75° Abs., is calculated. The refractive index of gaseous and liquid nitrogen at the boiling point has also been determined. In the case of the gas, the following values have been obtained at 752·32 mm. and 77·97° Abs.; $\lambda=643·9$, $n=1·0010779$, $\lambda=546·1$, $n=1·0010847$, $\lambda=435·8$, $n=1·0011007$, whilst the liquid at 745·12 mm. and 77·12° Abs. gave the values $\lambda=656·3$, $n=1·19844$; $\lambda=579·1$, $n=1·19876$, $\lambda=546·1$, $n=1·19918$, $\lambda=435·8$, $n=1·20142$; $\lambda=404·7$, $n=1·20258$. Wiener has replaced the figure 2 of the Lorenz-Lorentz formula by the symbol u, which he terms the form number. The value of u is exactly 2 for substances the molecules of which are exactly spherical, but is greater than 2 if the form diverges from the spherical. In the present case, the value of u has been calculated from the formula $(n_L^2-1)/(n_L^2+u)/d_L=(n_g^2-1)/(n_g^2+u)\cdot d_g$, in which d_L and d_g are the densities of the liquid and gas at the boiling point and n_L and n_g the respective refractive indices, and the mean value $u=2·16\pm0·04$ obtained. This value indicates that the nitrogen molecule behaves as though it were nearly spherical, but since for red light $u=2·04$, it behaves as though more nearly spherical than in the case of violet light, where $u=2·26$. Consequently it follows that the electron which is active in the absorption of light of short wave-length has a greater orbit than that operative in the absorption of light of longer wave-length.

J. F. S.

The Attack of Metals by Sulphuric-Nitric Acid Mixtures. PAUL PASCAL [with GARNIER and LABOURRASSE] (*Bull. Soc. chim.*, 1921, [iv], **29**, 701—709).—An examination of the action of mixtures of sulphuric and nitric acids varying in proportion and concentration on aluminium, steel, and lead, the results being expressed as loss in weight of the metal in grams per square metre in twenty-four hours, a large excess of the acid being used, and the temperature being maintained at 16—18° for the aluminium and steel and 19—21° for the lead. The addition of sulphuric acid to nitric acid facilitates the attack of aluminium. With nitric acid alone, the presence of ammonium nitrate slightly increases the attack of the metal. For all the varying proportions of sulphuric and nitric

acids, there is a concentration corresponding with between 10 and 20% of water at which the resistance of steel is a maximum.

W. G.

Fusion of Carbon. SIEGMAR MÜNCH (*Zeitsch. Elektrochem.*, 1921, **27**, 367—368).—On strongly heating graphite rods by means of a powerful electric current, they are shown to soften and become plastic and eventually to melt. A graphite rod 50 mm.^{2} in cross section and 5 cm. long, when subjected to a current of 800 amperes at 25 volts, melts and may be welded to a large graphite block which serves as a carrier for the current used. The plastic graphite may be bent or compressed so that its diameter is doubled. An apparatus is described by means of which large quantities of graphite may be melted. The cooled molten graphite has a metallic lustre. The literature dealing with previous attempts to melt carbon is considered. (See following abstract.) J. F. S.

[**Fusion of Carbon**]. EUGEN RYSCHKEWITSCH (*Zeitsch. Elektrochem.*, 1921, **27**, 368—369; cf. preceding abstract).—A criticism of statements made by Münch in connexion with the author's experiments on the fusion of carbon. It is pointed out that the large current (800 amperes) found necessary by Münch to fuse carbon was probably due to the experiment being carried out in the open air, where the cooling was very great. This also accounts for the very few drops of molten carbon obtained, since graphite burns in air at 900°. J. F. S.

The Action of Alkaline Hydrogen Peroxide on Silver [Nitrate] Solution and the Behaviour of Silver towards Dilute Sulphuric Acid. E. SALKOWSKI (*J. pr. Chem.*, 1921, **102**, 194—208).—When silver nitrate solution is added gradually to a dilute solution of hydrogen peroxide containing a little potassium or sodium hydroxide, a black precipitate is formed initially which becomes greyer as more of the silver nitrate solution is added, and ultimately resembles elementary silver. Analysis, however, shows it to be a mixture of silver and silver oxide in which the proportion of the former increases with increasing quantities of hydrogen peroxide in the solution. Silver peroxide is not present. Analysis is effected by treating the product with boiling dilute sulphuric acid (100 grams of acid made up to a litre with water), which almost completely dissolves the oxide, but only attacks metallic silver to a very slight extent. (The reason of this slight solvent action could not be elucidated; it does not appear to depend on the presence of atmospheric oxygen, nor does sulphur dioxide seem to be liberated during the process.) The black colour of the precipitate is therefore due to the presence of a black modification of silver which can be prepared in a very stable condition by adding a solution of silver nitrate (3%, 10 c.c.) to a solution of dextrose (10%, 20 c.c.) and sodium hydroxide (*d* 1·16, 5 c.c.).

Silver peroxide may be detected in the following manner. A small portion of the substance is heated to boiling for a short time

with an aqueous solution of an aliphatic amino-acid, preferably glycine or alanine, which must not be used in too small quantity. The formation of a silver mirror indicates the presence of silver peroxide, whereas silver oxide does not show this reaction. Also, when silver peroxide is covered with nitric acid (d 1·2) a dark brown solution is produced which becomes lighter and finally colourless when heated, but retains its colour for days at the laboratory temperature. The second test appears to be somewhat more sensitive than the first. H. W.

Decomposition of Ammonium Carbonate with Calcium Sulphate. BERNHARD NEUMANN [with WALTER GELLENDIEN] (*Zeitsch. angew. Chem.*, 1921, **34**, 441—442, 445—447).—The author has investigated theoretically the reaction between ammonium carbonate and calcium sulphate. The latter substance forms two hydrates and exists in three anhydrous forms. Although there is uncertainty as to absolute solubilities, it is known that the dihydrate, gypsum, has a maximum solubility at about 38° and that the most soluble form is the semihydrate, for which the figure may reach 1%. The dihydrate has a negative heat of solution, the other forms have positive heats.

It is calculated that the yield of ammonium sulphate with $0·25N$-ammonium carbonate solution should be 99·97%, the value rising slightly with increasing concentration. The yield at any temperature is calculated from the equation

$$\log_e K_1/K_2 = 2·303 \log K_1/K_2 = -Q/R \,.\, T_2 - T_1/T_1 - T_2$$

where Q is the heat of solution of calcium sulphate, that of the carbonate being negligible. It is shown that the influence of temperature on the reaction equilibrium is slight.

Experiments showed that in all cases conversion was almost complete in an hour, but complete equilibrium was only reached in from fifteen to twenty hours. The maximum yields obtained were: for the dihydrate 85%, for the semihydrate and gypsum heated at 200—300° 92%, and for anhydrite 90%. In all cases the yields increased slightly with the concentration of the ammonium carbonate solution. The yield with the dihydrate increased with the temperature up to 38°, and then remained constant. Owing to the decomposition of ammonium carbonate at 58°, heating beyond this point is useless. Change of temperature had no appreciable effect on the reaction with ignited gypsum. The discrepancy between these results and the theoretical yields of more than 99% was explained by determining the solubility curve of calcium sulphate in ammonium sulphate solutions of different strengths; the existence of a double salt, $(NH_4)_2SO_4,CaSO_4,H_2O$, was indicated. The suggestion that the reaction might be further complicated by an appreciable solubility of calcium carbonate in ammonium carbonate solution was investigated and disproved. C. I.

Decomposition of Calcium Sulphate by Ammonium Hydroxide. BERNHARD NEUMANN [with GERTRUD KOTYGA] (*Zeitsch. angew. Chem.*, 1921, **34**, 457—459).—Equilibrium conditions in the reaction $2NH_4{\cdot}OH + CaSO_4 \rightleftarrows (NH_4)_2SO_4 + Ca(OH)_2$

were investigated. If $Lm_1\alpha$ and $2Lm_1\beta$ are the concentrations of the ions [SO_4] and [OH], the ratio of the molecular solubilities of the products [Ca]·[SO_4] and [Ca]·$[OH]^2$ is $Lm_1^2\alpha^2/4Lm_1^3\beta^3$, which ratio, k, is found to be 3821 at 18°. If x and y are the molecular ionic concentrations and a is the normality of the ammonia solution $x/y^2=k$ and $2x+y=a$, k being known, y is determined in terms of a and the yield for any concentration of ammonia thus obtained. It varies from 6·6% with N/100-ammonium hydroxide to 88% with 10N-solution. The variation with temperature may also be calculated; up to 37° the yield falls. The reaction was experimentally investigated by shaking two flasks, one containing gypsum and water and the other gypsum and ammonium hydroxide solution, and estimating the sulphate in solution in each from time to time. For N/10-ammonium hydroxide, the yield was 33%, in agreement with the calculation, but with increasing concentration it fell rapidly instead of rising, with N-solution being only 3%. The reaction is thus useless for practical purposes. The reverse reaction, $(NH_4)_2SO_4+Ca(OH)_2=(NH_4)OH+CaSO_4$, gave a 96% decomposition with 5N-ammonium sulphate solution, falling to 53% with N/4-solution. The latter is again in agreement with calculation; the figures for stronger solutions are in excess of those to be expected. All these divergencies occurring in all solutions except the weakest, are due to the varying solubilities of calcium sulphate in ammonium sulphate solutions caused by the formation of the double salt. C. I.

The System Potassium Sulphate–Glucinum Sulphate–Water at 25°. HUBERT THOMAS STANLEY BRITTON and ARTHUR JOHN ALLMAND (T., 1921, **119**, 1463—1470).

Phosphorescent Zinc Sulphide. RUDOLF TOMASCHEK (*Ann. Physik,* 1921, [iv], **65**, 189—215).—A method is described whereby phosphorescent zinc sulphide may be prepared so that a product of uniform and reproducible properties for the examination of the phosphorescence of this substance is now for the first time obtained. Using this method, zinc sulphide containing respectively manganese and copper as phosphorogens has been prepared, and the properties and the phosphorescence bands of these substances have been examined. The bands have been compared with those previously obtained with ill-defined material. The phosphorescence phenomena of zinc sulphide containing respectively bismuth, lead, silver, uranium, nickel, and cobalt have been examined, and a number of new phosphorescence bands found and measured. The whole of the bands are considered and the series nature pointed out.

J. F. S.

Corrosion of certain Complex Brasses in Sea-water. I. L. BELLADEN (*Gazzetta,* 1921, **51**, ii, 144—159).—Of three samples of delta metal examined, that showing the greatest resistance to the corrosive action of sea-water contains the highest proportions of lead, manganese, and iron, as well as a small percentage of

nickel, which is lacking in the other two. [Cf. *J. Soc. Chem. Ind.*, 1921, 701A.] T. H. P.

The Theory of Smelting. III. Equilibria between Pairs of Metals and Sulphur. The System, Copper–Antimony–Sulphur. W. GUERTLER and KARL LEO MEISSNER (*Metal u. Erz*, 1921, **18**, 410—415).—It is shown that sulphur cannot exist in equilibrium with copper antimonide and that a reaction occurs with the formation of cuprous sulphide. $2Cu_3Sb+S=2Cu_2Sb+Cu_2S$; $Cu_2Sb+S=Cu_2S+Sb$. Cuprous sulphide melted with either antimony or the antimonides yields stable mixtures, but no ternary compounds are formed. Copper and antimony trisulphides react according to the equations: $12Cu+Sb_2S_3=3Cu_2S+2Cu_3Sb$; $10Cu+Sb_2S_3=3Cu_2S+2Cu_2Sb$; $6Cu+Sb_2S_3=3Cu_2S+2Sb$. The rectangle $Cu-Sb-Sb_2S_3-Cu_2S$ is subdivided into six triangles by the five quasi-binary intersections, Cu_2S-Cu_3Sb; Cu_2S-Cu_2Sb; Cu_2S-Sb; Cu_3SbS_3-Sb; and $CuSbS_2-Sb$. Two independent mixture gaps occur in the system, which are probably dependent on similar gaps in the binary systems $Cu-Cu_2S$ and $Sb-Sb_2S_3$. J. F. S.

Electrolysis of Cerium Salts in Aqueous Solutions. A. B. SCHIØTZ (*Tidskrift Kem.*, 1920, **17**, 213—215, 228—232).—The double chlorides of cerium and iron were electrolysed in an aqueous solution in presence of lactic acid, the rotating, dome-shaped, lead-plated platinum cathode being inverted over the anode chamber; the latter consisted of a glass tube with a helical row of openings, the platinum wire anode being wound round the tube through which the anode liquid was drained. The product consisted of a cerium–iron alloy containing 59·4 to 67% of cerium, and was probably free from oxides. CHEMICAL ABSTRACTS.

Aluminium. E. RATTENBURY HODGES (*Chem. News*, 1921, **123**, 141).—Aluminium foil is unattacked by boiling strong acetic acid even after eighteen days in the absence of air; on exposure to the air for a week, traces of aluminium were found to have dissolved. If, however, a few drops of hydrogen peroxide are added to strong acetic acid in which a strip of the metal is immersed, the whole dissolves at 15° within thirty hours. Slightly warmed aluminium foil reacts with bromine with brilliant incandescence, the mixture evolving a heavy grey vapour of anhydrous bromide and leaving a brown, granular residue which soon deliquesces to a liquid from which colourless tabular crystals may be obtained on evaporation. Whilst citric and tartaric acids have no effect on the metal, oxalic acid dissolves it very slowly in the cold but more readily on heating, the solution, on evaporation, yielding an oily-looking colloidal film which deliquesces in moist air. Strong phosphoric acid readily dissolves aluminium foil, whereas it has no action on tin foil; this difference serves to distinguish between the two elements. A. R. P.

Equilibrium Diagram of the System, Silicon–Iron. TAKEJIRÔ MURAKAMI (*Sci. Rep. Tôhoku Imp. Univ.*, 1921, **10**, 79—92).—Silicon–iron alloys containing up to 32·7% of silicon

have been prepared and subjected to magnetic, thermal, and microanalysis and the equilibrium diagram has been constructed. It is shown that there are two compounds, Fe_3Si_2 and FeSi, in the system. The former is magnetic with its critical point at 90°, whilst the latter is non-magnetic. An alloy corresponding with the formula Fe_2Si (20% Si) is neither a compound nor a saturated solid solution, as stated by Tammann and Guertler (A., 1906, ii, 32). The compound Fe_3Si_2 dissolves in iron up to 16% of silicon at ordinary temperatures. The critical point of its solid solution in iron gradually decreases from 790° to 450°, as the silicon content increases from 0 to 16%. As the temperature rises, the solubility increases to 23% of silicon at 1020°. By heating to a temperature above 1100°, the compound Fe_3Si_2 dissociates into iron and FeSi, and in alloys containing more than 23% of silicon, FeSi separates primarily on cooling the melt, and at 1020° Fe_3Si_2 is formed. Photomicrographs of sections of a large number of alloys are appended to the paper. J. F. S.

Mineralogical Chemistry.

The Structure of Humic Acids and Coals. J. MARCUSSON (*Zeitsch. angew. Chem.*, 1921, **34**, 437—438).—The author criticises the assumption of Fischer and Schrader (this vol., ii, 210) that natural humic acids are phenolic in character and contain no furan ring, basing their conclusions on the effects of oxidation under pressure. Lignin, natural humic acids, lignite, and coal yield benzenecarboxylic acids, whilst cellulose and artificial humic acids from carbohydrates yield furancarboxylic acids. Chardet (*Rev. gen. Chim. pure appl*, **17**, 214) has shown, however, that the dry distillation of natural humic acids yields both furan and furfuraldehyde in addition to phenolic compounds. Fischer and Schrader have recently (*Brennstoff-Chem.*, 1921, **2**, 216) obtained furancarboxylic acids as well as benzenecarboxylic acids by the oxidation under pressure of artificial humic acids obtained by treating sugar with strong hydrochloric acid. If humic acids contain a *peri*-difuran ring (this vol., i, 313), this, on decomposition, would yield derivatives of either benzene or furan, according to the experimental conditions. Succindialdehyde is considered to be an intermediate product in the formation of humic acid from furan. An aldehyde acid (Humalsäure), closely related to humic acid, has been recently found in peat, but it is not found in lignite. The *peri*-difuran nucleus exists in coal and lignite, the presence of the bridged oxygen being proved, as with humic acid, by the behaviour with fuming sulphuric acid or with nitric acid, and the formation of double salts with iron chloride and with mercury bromide. The

author concludes that both cellulose and lignin have taken part in the formation of coal. W. P.

Analytical Chemistry.

Micro-analysis of Gases by the Use of the Pirani Pressure Gauge. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD. (N. R. CAMPBELL) (*Proc. Physical Soc.*, 1921, **33**, 287—296).—A method of analysis of small quantities of gases is described. The method consists in determining the condensation temperature of each gas consecutively. The gas contained in a side tube of a Pirani gauge is cooled to a temperature sufficient to liquefy the whole mixture, or, if some non-condensible gas is present, until the whole liquefiable portion has been liquefied. The temperature is then slowly raised and pressure–temperature readings are taken. A curve is produced which consists of a number of horizontal lines of constant pressure joined by a number of vertical, or nearly vertical, lines of constant temperature. The vertical temperature lines give the condensation temperatures of the individual constituents. The length of the ordinates serves as a relative measure of the quantity of each constitutent. The total pressure admissible in the determination is 0·2 mm. and measurements may be made down to 0·001 mm. As cooling bath, the authors recommend freezing mercury (—39°), freezing chloroform (—65°), freezing acetone (—95°), freezing ethyl alcohol (—117°), and liquid air (—183°). In actual practice no thermometer is used, but the condensation temperatures of the mixture are compared with the condensation temperatures of the individual gases. To do this a number of gauges are made each containing one pure gas, and these are observed alongside the gauge containing the mixture. The method is very accurate and capable of wide application.

J. F. S.

Losses in Chlorine in the Estimation of Chlorine in Organic Compounds by Incineration and their Prevention. A. WEITZEL (*Arb. Reichs-Gesundh.-Amt*, 1920, **52**, 635—649; from *Chem. Zentr.*, 1921, iv, 228).—The ordinary methods for the estimation of chlorine in organic compounds by incineration are examined. The most suitable is the author's wet method (A., 1917, ii, 501). By observing certain precautions, however, chlorine can be estimated in the ash of organic compounds. Accurate results may be obtained if the substance is mixed with limé and water to form a cream, which is then dried and incinerated; or the substance may be incinerated after mixing with sodium carbonate and potassium nitrate.

G. W. R.

The Estimation of Bromine in Salt Waters. P. LEBEAU and M. PICON (*Bull. Soc. chim.*, 1921, [iv], **29**, 739—743).—A preliminary approximate estimation is made by titrating 1 c.c. of

the water with chlorine water containing 0·5 gram of chlorine per litre until decoloration just commences. The volume required represents approximately double the amount of chlorine required to displace all the bromine present as bromide.

A volume of water containing about 0·1 gram of bromine is placed in a separating funnel, 5 c.c. of 10% hydrochloric acid are added, and the calculated quantity of chlorine water containing 5 grams of chlorine per litre is run in. The liberated bromine is extracted with 15 c.c. of chloroform, and the chloroform extract is run into 10 c.c. of 10% potassium iodide solution in a stoppered bottle. The liquid in the separating funnel is again extracted with chloroform after the addition of 0·3—0·5 c.c. of chlorine water. This is repeated until the chloroform is colourless. The iodine liberated by the addition of the chloroform extracts to the potassium iodide is titrated with *N*/10-sodium thiosulphate. To obtain satisfactory results by this method the use of excess of chlorine water must be avoided, and the volume of water containing 0·1 gram of bromine as bromide should not exceed 25 c.c., a preliminary evaporation being conducted if necessary. W. G.

Volumetric Estimation of Sulphurous Acid in Organic Substances by Distillation. VICTOR FROBOESE (*Arb. Reichs-Gesundh.-Amt*, 1920, **52**, 657—669; from *Chem. Zentr.*, 1921, iv, 225).—The method proposed is a modification of that of Haase (A., 1882, 773). The sulphur dioxide obtained by distillation is collected in a standard solution of sodium hydrogen carbonate in the presence of hydrogen peroxide, whereby the sulphite is oxidised to sulphate. The excess of sodium hydrogen carbonate is titrated with hydrochloric acid, using methyl-orange as indicator. The sulphate formed may be estimated gravimetrically by precipitation with barium chloride as a control. The water used for the dilution of the liquid from which the sulphur dioxide is distilled must be free from oxygen. A long reflux condenser is desirable in order to prevent volatile organic acids from passing over. The method is applicable to the estimation of sulphites in cellulose–sulphite liquors, wine, dried fruit, and gelatin. G. W. R.

Volumetric Method for the Estimation of Acids and Bases which yield Insoluble Salts. G. BRUHNS (*Zeitsch. anal. Chem.*, 1921, **60**, 224—229).—A method described previously by Bucherer (A., 1920, ii, 702) yielded trustworthy results in the estimation of sulphates in crude sugars, molasses, etc.; the separation of the precipitated barium sulphate is facilitated by the addition of a small quantity of aluminium hydroxide, which, when kept for two days, becomes particularly insoluble in acid solutions. W. P. S.

Modification of the Dumas Method, and Application of the Kjeldahl Method to the Estimation of Nitrogen in Nitronaphthalenes. PAUL H. M.-P. BRINTON, F. N. SCHERTZ, W. G. CROCKETT, and P. P. MERKEL (*J. Ind. Eng. Chem.*, 1921, **13**, 636—639).—In the modified Dumas method described, the carbon dioxide used is generated from dilute sulphuric acid and sodium

carbonate solution which are admitted to a large container filled originally with water; the gas is passed through two measuring bottles, one of which is filled with water, and the discharge of this from one bottle to the other, alternately, indicates the volume of carbon dioxide passing. The gas is then conducted, by a suitable arrangement of tubes and three-way taps, to the combustion tube, where the substance is burnt with copper oxide. The nitrogen is collected over sodium hydroxide solution, three nitrometers being used in connexion with each other; the combustion gases pass upwards through the first nitrometer, causing a circulation of sodium hydroxide solution from this to the others, and the liquid collecting in the levelling bulbs is returned to that of the first nitrometer as required. One of the nitrometers is provided with a water-jacket, and serves as the measuring vessel for the nitrogen.

To estimate nitrogen in nitronaphthalenes by the Kjeldahl method, about 0·5 gram of the substance is heated with 30 c.c. of sulphuric acid and 2 grams of salicylic acid for two hours on a water-bath, the mixture is then cooled, 2 grams of zinc dust are added, and after about eighteen hours the mixture is heated, first at 70°, and afterwards over a small burner, until all visible action ceases. One gram of mercuric oxide is next added, the mixture boiled for one hour, cooled, 7·5 grams of potassium sulphate are added, and the boiling is continued for a further period of one hour. The ammonia is then estimated by distillation in the usual way. The results obtained are lower than those found by the Dumas method, the difference increasing with the nitrogen content. For instance, 13·74% of nitrogen found by the Kjeldahl method corresponds with 14·33% by the Dumas method, and 15·48% with 16·85%. W. P. S.

Micro-estimation of Nitrogen and its Biological Applications. M. Polonovski and C. Vallée (*J. Pharm. Chim.*, 1921, [vii], **24**, 129—134).—To estimate the total nitrogen, a portion of the substance containing from 1 to 2 mg. of nitrogen is heated for fifteen minutes in a test-tube with 1 c.c. of sulphuric acid and 1 gram of potassium sulphate. The mixture is then diluted with 6 c.c. of water, and the tube is connected with a small absorption vessel containing $N/50$-sulphuric acid; a current of air, heated previously by passing it through warm water containing a small quantity of sulphuric acid, is aspirated through the whole apparatus. After twenty minutes, the absorption apparatus is disconnected and the excess of sulphuric acid is titrated. Another portion of 3 c.c. of the original solution is then treated with 2 drops of acetic acid and a small quantity of sodium chloride, the mixture is heated at 90°, cooled, submitted to centrifugal action, and the nitrogen determined in an aliquot portion of the clear liquid; the difference between the two estimations gives the amount of nitrogen present as coagulable albumin. W. P. S.

Removal of Protein from Body Fluids for the Purpose of Simultaneous Estimation of Many Constituents. Genko Mukai (*Biochem. J.*, 1921, **15**, 516—520).—For the estimation of

non-protein nitrogen in serum, etc., the author boils the substance with sodium acetate and acetic acid, and removes the last traces of protein with talcum. The results are usually very slightly higher than those of the Folin-Denis method (A., 1912, ii, 703). G. B.

Estimation of Sodium Nitrite. F. MUHLERT (*Zeitsch. angew. Chem.*, 1921, **34**, 448).—In the estimation of nitrites by the diazotisation method, *o*-aminobenzoic acid may be advantageously substituted for sulphanilic acid. The end point is sharp, the diazo-compound stable, and the reagent can be easily obtained in a pure state. C. I.

Source of Error in the Estimation of Nitrate-Nitrogen by Ulsch's Method. F. MACH and F. SINDLINGER (*Zeitsch. anal. Chem.*, 1921, **60**, 235—238).—Traces of sulphide in the reduced iron used for the reduction of nitrates according to Ulsch's method cause the results obtained to be much too low. For instance, a potassium nitrate solution containing 13·86% of nitrogen yielded only 12·90% when the reduction was carried out with iron containing 0·03% of sulphur as sulphide. Each new quantity of reduced iron should, therefore, be tested against a pure nitrate before it is used for actual estimations. W. P. S.

Estimation of Phosphorus in Iron, Steel, Ores, and Slags. H. KINDER (*Zeitsch. anal. Chem.*, 1921, **60**, 241—257).—A report of a critical examination of the molybdate method for the estimation of phosphorus, with particular reference to the influence of other elements. In the estimation of phosphoric acid in slags, the magnesium pyrophosphate method yielded results which were slightly higher (0·1 to 0·3%) than those yielded by the molybdate method. W. P. S.

Double Arsenic Tubes. GEORG LOCKEMANN (*Zeitsch. angew. Chem.*, 1921, **34**, 396).—To economise in glass tubing, a piece of hard glass tubing is drawn out so that three portions of the original diameter of the tube are connected by capillaries, the whole being in one piece; the tube is used in conjunction with the ordinary Marsh apparatus. The first arsenic mirror is obtained in the first capillary; for the next estimation, the second wide portion and capillary are used, and the tube is then reversed and used in a similar manner for two further estimations. W. P. S.

Micro-estimation of Carbon Monoxide in Blood. MAURICE NICLOUX (*Bull. Soc. Chim. Biol.*, 1921, **3**, 286—296).—A micro-modification of the author's method (A., 1921, i, 204) for the estimation of carbon monoxide in blood is described; 2 to 5 c.c. of blood are used for an estimation, and it is claimed that the method is simple and accurate to within 2%. Notes are given on the application of the method to the estimation of the capacity of the blood for absorbing carbon monoxide, and of the amount of the latter present in blood in cases of poisoning. C. R. H.

Estimation of Metals in Alloys of Known Qualitative Composition. K. SCHMIDT (*Chem. Zeit.*, 1921, **45**, 825—826).—From a knowledge of the atomic weights and specific gravities of the constituent metals of a binary or ternary alloy, together with the weight and volume of the alloy under examination, it is possible to calculate the percentage composition. The author has obtained formulæ for binary and ternary alloys involving in the first case the use of four constants based on the atomic weights and specific gravities of the constituent elements and these have been calculated for all the more important commercial binary alloys. [Cf. *J. Soc. Chem. Ind.*, 1921, Oct.] A. R. P.

Estimation of Alkali Hydroxide and Carbonate in presence of Cyanide and Ferrocyanide. F. MUHLERT (*Zeitsch. angew. Chem.*, 1921, **34**, 447).—A method for the estimation of alkali in potassium or sodium cyanide consists in titrating the cyanide with silver solution, removing the turbidity formed at the end point with a drop of cyanide solution, and then titrating with normal acid until the turbidity reappears. The method is accurate if most of the alkali is present as hydroxide. In presence of other weak acids, for example, formic acid, this method cannot be used, neither does Clenell's method give good results. The best procedure is as follows. The cyanide is first titrated with silver solution, and the same quantity of solution added to another sample. The resulting solution after filtration can now be used for whatever alkalimetrical estimations are desired. If great accuracy is not required, the solution need not be filtered. If ferrocyanide is present, the solution may be titrated directly with normal acid and methyl-orange. The cyanide having been previously estimated, the alkali is obtained by difference. C. I.

Rapid Estimation of Silver in Alloys by a Modified Silver Chloride Method. SAUERLAND (*Chem. Zeit.*, 1921, **45**, 735—736).—About 0·5 gram of the alloy is treated with 10 c.c. of nitric acid, *d* 1·4, a small quantity of water is added, the mixture boiled, diluted to 80 c.c., again boiled, and, after five minutes, the insoluble matter (gold, tin, antimony) is collected on a filter and washed. A slight excess of hydrochloric acid is added, drop by drop, to the filtrate, the latter is then boiled, and the silver chloride is collected on a filter. The moist filter is then supported on the mouth of a small crucible, the upper part of the paper is wrapped round the end of a porcelain tube connected with a supply of coal gas, and the crucible is heated by a burner; the filter-paper chars, and after a time falls into the crucible, the silver chloride meanwhile being reduced by the coal-gas introduced through the porcelain tube. The reduction is completed by the incineration of the charred paper, and the resulting metallic silver is weighed. W. P. S.

Simple Technique for the Estimation of Calcium and Magnesium in Small Amounts of Serum. BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1921, **47**, 475—481).—One or 2 c.c. of serum, diluted with 2 c.c. of water, are mixed with

1 c.c. of saturated ammonium oxalate solution. The precipitate is collected by centrifuging and repeatedly washed in the same way with water and 2% ammonia, and is then titrated with $N/100$-potassium permanganate solution. An aliquot portion of the supernatant fluid of the calcium estimation is precipitated with ammonium phosphate; the ammonium magnesium phosphate is collected in a Gooch crucible and is dissolved in $N/100$-hydrochloric acid. Half the solution, mixed with 2 c.c. of a ferric thiocyanate solution, is compared colorimetrically with standards prepared with known amounts of ammonium magnesium phosphate. The error is $\pm 5\%$ of the calcium and magnesium present. G. B.

Sensitiveness and Applicability of Qualitative Reactions. II. Barium Ions. O. LUTZ (*Zeitsch. anal. Chem.*, 1921, **60**, 209—223; cf. A., 1920, ii, 509).—The following are the minimum quantities of barium which can be detected by various reagents; in each case, 5 c.c. of the barium salt solution were treated with 0·5 c.c. of the reagent and the observation was made after five minutes. Sodium arsenate and ammonium chloride, 1 : 175; potassium ferrocyanide and ammonium chloride, 1 : 430; ammonium oxalate, 1 : 4400; sodium phosphate, 1 : 6200; aniline hydrosilicofluoride, 1 : 6000; ammonium carbonate and ammonia, 1 : 28000; sodium carbonate, 1 : 160000; sodium sulphite, 1 : 160000; ammonium chromate, 1 : 1200000; sulphuric acid, 1 : 1600000. W. P. S.

Application of Amalgams in Volumetric Analysis. I. Estimation of Molybdenum, Titanium, and Iron. TAMAKI NAKAZONO (*J. Chem. Soc. Japan*, 1921, **42**, 526—537).—About 0·15 gram of the metallic compound is reduced by vigorously shaking with 200 grams of liquid zinc amalgam and 10 c.c. of $2N$-sulphuric acid during 0·5—1 minute in a specially made separating funnel, in which the air is replaced by carbon dioxide. After the reaction is completed, the solution is titrated with standard potassium permanganate solution. The method has been successfully applied to ammonium molybdate, titanic acid, and iron alum. The amalgam is prepared by heating 3 to 4 grams of zinc with 100 grams of mercury and some dilute sulphuric acid on a water-bath for one hour; the product is thoroughly washed with water and separated from solid residue. The amalgam may be used many times without loss of activity and the effect of some impurities in the metal on the accuracy is almost negligible. K. K.

Dimethylglyoxime Reactions of Iron and Cobalt. WILH. VAUBEL (*Zeitsch. öffentl. Chem.*, 1921, **27**, 163—164).—A deep red coloration is obtained when solutions of ferrous salts are treated with dimethylglyoxime solution and ammonia; the reaction is also given by ferric salts if a trace of ammonium sulphide is added before the ammonia. This coloration is distinct from that given by nickel salts, and there is no formation of a precipitate. Cobalt solutions give a yellowish-brown coloration with dimethylglyoxime

and ammonia; if ammonium sulphide is added before the ammonia, the coloration produced is bluish-violet to deep red.] W. P. S.

Quantitative Separation of Tin and Antimony in the Presence of Phosphoric Acid. (Mlle) Mouret and J. Barlot (*Bull. Soc. chim.*, 1921, [iv], **29**, 743—745).—The tin-antimony alloy is dissolved in aqua regia and the solution evaporated almost to dryness. The residue is taken up with warm concentrated hydrochloric acid and the solution diluted with an equal volume of water. To it is added at least 50 c.c. of an 8—9% solution of crystalline orthophosphoric acid for every 0·01 gram of tin present. The antimony is precipitated as sulphide by hydrogen sulphide at 80—90°, collected on a filter, and the antimony subsequently estimated electrolytically. The filtrate is boiled to remove hydrogen sulphide and the tin is precipitated by the addition of cupferron and estimated in the usual manner. W. G.

Estimation of Titanium in Iron and Steel. Theodor Dieckmann (*Zeitsch. anal. Chem.*, 1921, **60**, 230—234).—One gram of the sample and 1 gram of iron free from vanadium are dissolved separately in dilute nitric acid, the two solutions are evaporated with the addition of sulphuric acid and heated until fumes of sulphuric acid are evolved; after cooling, the residues are boiled with dilute sulphuric acid, silica is separated by filtration, and the filtrates are treated with 10 c.c. of phosphoric acid (*d* 1·3) and a few c.c. of hydrogen peroxide. Standard titanium sulphate solution is added to the solution containing the iron free from vanadium until the colour of this solution is brought to the same intensity as that of the solution containing the sample under examination. W. P. S.

Estimation of Nickel and Copper on Nickel-plated or Copper-plated Iron Articles. H. Koelsch (*Zeitsch. anal. Chem.*, 1921, **60**, 240—241).—The nickel or copper may be dissolved by immersing the metal in a hot sodium nitrite solution acidified with acetic acid; the iron does not dissolve as long as nitrite ions are present (see D.R.-P. 319855 and 330131). W. P. S.

Estimation of Vanadium in Steels and Iron Alloys. Luigi Rolla and Mario Nuti (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 287).—Vanadium may be precipitated quantitatively from a solution containing about 1% of free hydrochloric or sulphuric acid by means of 4% aqueous "cupferron" solution in the cold, the precipitate being washed with 2% hydrochloric or sulphuric acid solution to which 2% of the 4% cupferron solution has been added, dried at about 70°, calcined and weighed as vanadium pentoxide. Iron and chromium may be easily separated from vanadium by precipitation by means of boiling sodium hydroxide solution. In the case of ferrovanadium, about 0·5 gram is treated with six times its weight of sodium peroxide in an iron crucible, the silica being removed after filtration and the iron as described above, and the

vanadium precipitated with cupferron. With steel, the hydrochloric acid solution is used, this being freed from silica and tungsten by filtration and from iron by treatment with ether; the liquid is boiled with sodium carbonate and filtered, the filtrate being treated with either lead acetate or lead nitrate and acetic acid. The lead vanadate thus precipitated is dissolved in dilute hydrochloric acid and evaporated with concentrated sulphuric acid. The residue is taken up in water and the vanadium precipitated in the filtrate by means of cupferron. T. H. P.

Denigès's Test for the Detection and Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol. ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1921, **13**, 543—545).—A modification of Denigès's method is described, the new procedure rendering the test more trustworthy. The alcohol is diluted until it contains 1% of total alcohols (solution *A*); 10 c.c. of this solution are mixed with 10 c.c. of 4% ethyl alcohol and diluted to 50 c.c. (solution *B*), and 10 c.c. of the latter solution are also mixed with 10 c.c. of 4% ethyl alcohol and diluted to 50 c.c. (solution *C*). Four c.c. of each of these solutions are placed in separate Nessler cylinders, and standards containing 1, 2, 3, etc., c.c. of 0·04% methyl alcohol solution, and 1 c.c. of 4% ethyl alcohol solution are prepared in other cylinders, the volumes in each case being diluted to 4 c.c. Each cylinder then receives the addition of 1 c.c. of phosphoric acid (1 : 5) solution and 2 c.c. of 3% potassium permanganate solution; after thirty minutes, 1 c.c. of 10% oxalic acid solution is added to each, followed, after two minutes, by 1 c.c. of concentrated sulphuric acid and 5 c.c. of Schiff-Elvove reagent. The colorations obtained are compared after the lapse of one hour. Acetone does not interfere with the method, but glycerol, carbohydrates, formic acid, acetic acid, and phenol, if present, should be removed by distilling the alcohol with the addition of sodium hydroxide; formaldehyde and terpenes are removed by treatment with silver nitrate and sodium hydroxide followed by distillation. W. P. S.

Possible Improvements in the Ebulliometric Estimation of Alcohol in Wines. UGO PRATOLONGO (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 290—293).—The construction of the scale, and the construction, control, and use of the ebulliometer, are discussed [see *J. Soc. Chem. Ind.*, 1921, 711A]. T. H. P.

Application of the Determination of Miscibility Temperature to Alcoholimetry. H. ROSSET (*Ann. Chim. Analyt.*, 1921, [ii], 3, 235—239).—The miscibility temperature (the point at which the surface of separation of certain mixtures disappears) may be used to estimate the alcoholic strength of a liquid. For instance, when 5 c.c. of an alcoholic solution are mixed with 30 c.c. of pure acetone and 5 c.c. of standard light petroleum (b. p. 210—225°), the miscibility temperature varies from $-5{\cdot}5°$ for 90% alcohol to $+27{\cdot}6°$ for 65% alcohol. For lower alcoholic strengths,

a mixture of 50 c.c. of acetone and 5 c.c. of light petroleum is used, 5 c.c. of the alcoholic solution being added; in this case, the miscibility temperature varies from $-1·0°$ for 65% alcohol to $+23·0°$ for 28% alcohol. W. P. S.

Concentration and Purification of Alcoholic Fermentation Liquids. I. Distillation in Steam of certain Alcohols. JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dubl. Soc.*, 1921, **16**, 233—247).—The distillation constants of methyl, ethyl, propyl, *n*-butyl, *iso*butyl and *sec.*-butyl, and *iso*amyl alcohols have been investigated under experimental conditions similar to those employed in the recent work on fatty acids (A., 1919, ii, 528). Dilute solutions of the alcohols were distilled at constant volume, in most cases 200 c.c., water being introduced into the distillation flask at the same rate as distillation proceeded. The alcohol content of successive fractions of distillate was estimated from the density and by oxidation. The distillation constant, $A=1/v \log a/a-x$, in which a is the initial amount of alcohol in the flask and x the amount in the total distillate after a volume v has distilled, was found to increase with the molecular weight of the alcohols and to be greater for *sec.*- and *iso*-butyl alcohols than for *n*-butyl alcohol. For a given alcohol it was, as anticipated from general considerations, inversely proportional to the initial volume of liquid in the flask, and it also varied, although to a smaller extent, with the concentration of the alcohol, increasing as the concentration diminished. This variation of the constant with concentration confirms earlier work by Sorel (A., 1893, ii, 347) and Gröning. Several possible causes of these variations are discussed, and it is suggested that they may be accounted for by variations in the "mass of water per c.c. of distillate." J. H. L.

Estimation of Cresol by the Phenol Reagent of Folin and Denis. ROBERT M. CHAPIN (*J. Biol. Chem.*, 1921, **47**, 309—314).—Apart from other defects (cf., for example, Gortner and Holm, A., 1920, ii, 643), the estimation of phenols by the colorimetric method of Folin and Denis (A., 1915, ii, 802) suffers from the disadvantage that the phenol reagent gives colours of different intensity with equivalent quantities of different phenols. For the estimation of total cresol in mixtures of cresols of approximately known composition the author therefore introduces the use of empirical factors. The method is applied to the estimation of phenolic preservatives in serums. E. S.

Volumetric Estimation of Aminonaphthol-mono- and disulphonic Acids. GIORGIO RENATO LEVI (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 297—302).—The aminonaphtholsulphonic acids may be titrated either with sodium nitrite in an acid solution or with diazo-compounds, comparison of the results obtained in these two ways serving as the best criterion of the purity of these compounds; the difference should be not more than 0·5% for a dry, or 0·2% for a pasty, product. The titration with nitrite is carried out by running $N/5$-sodium nitrite solution into a fresh solution or

suspension of the sulphonic acid containing free mineral acid; excess of the latter causes no appreciable increase in the velocity of diazotisation; the latter is, however, affected by the temperature, which should be to 10—12° at first and 25—30° at the end of the reaction. In the titration with diazo-compounds, the author makes use of either freshly-prepared diazobenzene or recently-titrated *p*-nitrodiazobenzene. In general, these aminonaphthol-sulphonic acids may undergo combination in two different ways, namely, in acid solution in the ortho-position to the amino-group, and in alkaline solution in the ortho-position to the hydroxyl group. Contrary to the statement made in many patent specifications, in acetic acid solution the combination occurs in the ortho-position with respect to the hydroxyl group. The colorations produced by the diazo-compounds of the aminonaphtholsulphonic acids are due to an internal combination, occurring either within a single molecule or between two molecules.

The aminonaphtholmonosulphonic acids examined were: M-acid ($NH_2 : OH : SO_3H = 1 : 5 : 7$), S-acid (1 : 8 : 4), γ-acid (2 : 8 : 6), J-acid (2 : 5 : 7) and R-acid (2 : 3 : 6), and the disulphonic acids: 2S-acid ($NH_2 : OH : SO_3H : SO_3H = 1 : 8 : 2 : 4$), H-acid (1 : 8 : 3 : 6), K-acid (1 : 8 : 4 : 6) and 2R-acid (2 : 8 : 3 : 6). Taking the "nitrite number" as basis, the titration of the diazo-compounds may be effected as follows: M-, 2S-, and 2R-acids with *p*-nitrodiazobenzene in sodium carbonate solution, and J- and R-acids in acetic acid solution; S-, γ-, and K-acids in acetic acid solution, and H-acid in sodium carbonate solution, with diazobenzene. Qualitative characters for the differentiation between the various isomerides are given. T. H. P.

The Estimation of Citronellol by the Formylation Method. ALEXANDER ST. PFAU (*J. pr. Chem.*, 1921, **102**, 276—282).—The estimation of geraniol and citronellol by the formic acid method gives inexact results, in part because a portion of the geraniol undergoes esterification. Even with pure citronellol, however, the method gives uncertain data (cf. Schimmel & Co., A., 1914, i, 67; Simmons, A., 1916, ii, 117). The author's results are irregular and high when 100% acid is used, but low with a weaker acid. It is shown that the action of the acid on citronellol is not a simple process, fractionation of the product under diminished pressure leading to the isolation of citronellyl formate, b. p. 99—100°(corr.)/7 mm., the compound, $OH\cdot CMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH_2\cdot O\cdot CHO$, b. p. 129°(corr.)/5 mm., d^{15} 0·9651, $\alpha_D + 1° 46'$, n_D^{15} 1·4488 and the corresponding *di-formate*, $CMe_2(O\cdot CHO)\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH_2\cdot O\cdot CHO$, a colourless, highly refractive liquid, b. p. 140—141°(corr.)/7 mm., unchanged citronellol and, frequently, a small amount of more volatile liquid, possibly an aliphatic or a cyclic terpene. H. W.

Estimation of the Composition of Ternary Mixtures: Ether–Water–Alcohol. LOUIS DESVERGNES (*Mon. Sci.*, 1921, **11**, 145—150).—The composition of mixtures of ethyl ether, ethyl alcohol, and water is estimated by determining the quantity of water or of ether required to produce a turbidity, or the quantity

of alcohol required to produce a clear liquid when the mixture is not homogeneous; graphs are given which show the composition corresponding with the quantities of water, etc., added.

W. P. S.

The Estimation of Sugar in Urine. J. C. VAN DER HARST and C. H. KOERS (*Pharm. Weekblad*, 1921, **58**, 1230—1232).—The fermentation apparatus devised by Stephan under the name hydrosaccharometer has been found to be more trustworthy than Wagner's apparatus and to give results as accurate as those obtained by the polarimeter where the sugar content is not below about 1%. The Causse-Bonnans method has been re-examined, and again found unsatisfactory.

S. I. L.

Volumetric Estimation of Phenylhydrazine and its Application to the Estimation of Pentosans and Pentoses. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1921, **15**, 466—468).—The carbohydrate is distilled in the usual way with 12% hydrochloric acid; an aliquot portion of the distillate is neutralised, slightly acidified, mixed with a standard aqueous phenylhydrazine solution (about 2%), kept at 50—55° for twenty minutes, and filtered; an aliquot part of the filtrate, containing excess of phenylhydrazine, is mixed with excess of standard iodine solution, and titrated with thiosulphate. The reaction is represented by the equation $PhNH{\cdot}NH_2+2I_2=3HI+C_6H_5I+N_2$. The results agree closely with those obtained by the phloroglucide method.

G. B.

Identification of Ouabain and Strophanthin, and a New Test to Distinguish between the two Glucosides. A. RICHAUD (*J. Pharm. Chim.*, 1921, **24**, 161—166).—To distinguish between ouabain and strophanthin in actual pharmaceutical practice where often only a milligram or so of the substances is available, the following differential characteristics may be utilised: Ouabain is soluble in 150 parts of water at 15°, whilst strophanthin dissolves in 40—43 parts at that temperature. The solution of the former is perfectly clear and colourless, and does not give a persistent froth on shaking. Strophanthin solutions, on the other hand, are inclined to be yellow, and are not perfectly transparent. They have a very pronounced bitter taste, and give a persistent froth on agitation. Under the microscope, ouabain appears as a pure white powder or small, rectangular tabular crystals, whilst strophanthin appears usually as a dirty or yellowish-white, amorphous powder, or crystallised in leaflets often grouped round a centre. Finally, a new colour reaction is proposed, which consists in warming in a water-bath at 60° or 70° in a test-tube 5 c.c. of concentrated hydrochloric acid, a few crystals of resorcinol, and a trace of the glucoside. Ouabain gives no coloration, and strophanthin a rose colour, the test depending, of course, on the difference in the sugars generated by the hydrolysis of the two glucosides.

G. F. M.

Detection of Oxalic and Citric Acids. M. POLONOVSKI (*J. Pharm. Chim.*, 1921, **24**, 167—168).—The usual method for the

detection of oxalic acid is simplified by the following procedure. The acid radicles are converted into sodium salts, and a saturated solution of calcium fluoride is added to the alkaline filtrate acidified with acetic acid. In presence of oxalic acid, calcium oxalate is precipitated under these conditions, its solubility in water at 15° being 0·00056%, whilst that of calcium fluoride is 0·05%. In the absence of fluorides from the original substance, a saturated solution of calcium sulphate may advantageously be substituted for the fluoride solution.

Citric acid may readily be detected in presence of any of the common organic acids by adding to the original solution potassium permanganate solution until the pink colour persists, then 1 c.c. of bromine water, and warming to decolorisation. In presence of citric acid, a precipitate of perbromoacetone is formed, but still more characteristic is the evolution of irritant vapours which attack the eyes, so that the least trace cannot possibly escape detection. G. F. M.

Detection and Estimation of Lævulic Acid in Foods. L. Grünhut (*Z. Unters. Nahr. Genussm.*, 1921, **41**, 261—279).—Lævulic acid occurs in certain carbohydrate foods, and is usually accompanied by formic, acetic, and lactic acids; it may be identified by the red coloration which it yields with sodium nitroprusside in alkaline or acetic acid solution. A method for the estimation of lævulic acid depends on its oxidation to acetic acid by means of potassium dichromate and sulphuric acid; the resulting acetic acid is distilled and titrated. Formic acid under the same conditions is oxidised to carbon dioxide; if the amount of acetic acid found in the distillate is in excess of that calculated from the quantity of dichromate reduced (after allowing for the formic acid as estimated separately by the mercuric chloride method), the presence of free acetic acid in the sample is indicated. Lactic acid is also oxidised by dichromate to acetic acid. In the case of a sample containing all the four acids mentioned, the procedure adopted is to acidify the substance with phosphoric acid, extract the organic acids with ether (a quantity of sodium hydroxide is placed in the extraction flask to prevent volatilisation of the formic acid with the ether), then extract the ethereal solution with dilute sodium hydroxide solution and evaporate the united aqueous extracts to dryness. The dry residue is dissolved in a definite volume of water, the organic acids are liberated, and the solution is submitted to a simple distillation. The distillate contains the whole of the acetic acid, the greater part of the formic acid, a small quantity of lævulic acid and no lactic acid; the residual solution in the flask will contain the greater part of the lævulic acid, the remainder of the formic acid, the whole of the lactic acid, and no acetic acid. The two solutions are analysed separately as described. W. P. S.

Detection and Estimation of Salicylic Acid in Wine. W. Fresenius and L. Grünhut (*Zeitsch. anal. Chem.*, 1921, **60**, 257—266).—Fifty c.c. of the wine are acidified with sulphuric acid,

extracted with a mixture of ether and light petroleum, the extract is evaporated, and the residue tested with ferric chloride. To estimate the salicylic acid, 500 c.c. of the wine are boiled under a reflux apparatus for one hour with the addition of sodium hydroxide solution, the mixture is then cooled, acidified with sulphuric acid, and extracted with ether–light petroleum mixture. The ethereal solution is evaporated with the addition of a small quantity of water, the residual aqueous solution diluted to a definite volume, and used for the colorimetric estimation of the acid by the ferric chloride method. W. P. S.

Estimation of Salicylates and Phenol. W. O. EMERY (*J. Ind. Eng. Chem.*, 1921, **13**, 538—539).—A method for the estimation of phenol and salicylates, particularly salol (phenyl salicylate), depends on the formation of a red, amorphous compound, di-iodo-phenylene oxide, when phenol or salicylic acid is treated with iodine in the presence of sodium carbonate: $2PhOH+6I_2+4Na_2CO_3=2C_6H_2OI_2+8NaI+4CO_2+4H_2O$, and $2C_6H_4(OH)\cdot CO_2H+6I_2+4Na_2CO_3=2C_6H_2OI_2+8NaI+6CO_2+4H_2O$. To estimate salol in admixture with acetanilide, phenacetin, and caffeine, a portion of the sample containing about 0·1 gram of salol is extracted with chloroform, the chloroform solution is evaporated, and the residue obtained treated with 10 c.c. of 1% sodium hydroxide solution and heated in a reflux apparatus at such a rate that it boils in two minutes; three successive quantities of 10 c.c., 30 c.c., and 50 c.c. respectively of water are then added, the mixture being boiled after each addition. One gram of sodium carbonate is added with the last quantity of water. An excess (55 to 60 c.c.) of $N/5$-iodine is then added to the boiling solution, the flask is removed from the condenser, a further 1 gram of sodium carbonate is introduced, and the mixture boiled gently for about twenty minutes. If phenacetin is present, the quantity of iodine solution mentioned should be increased by 5 c.c. for each 0·1 gram of phenacetin supposed to be in the mixture. The precipitate formed is collected, washed with 200 c.c. of hot water, dried at 100°, and weighed; the weight found is multiplied by 0·3113 to obtain the corresponding quantity of salol. W. P. S.

Estimation of the Saponification Number, Iodine–Bromine Number and Bromine-substitution Number [of Fats and Waxes]. E. SCHULEK (*Pharm. Zentr.-h.*, 1921, **62**, 391—395).—The use of propyl alcohol, as proposed by Winkler (A., 1911, ii, 550) is recommended in the estimation of the saponification number, since by the use of this solvent even waxes are saponified completely in a short time. In the case of the iodine–bromine number, the results obtained are the higher the longer the time of contact of the fat or oil with the reagent, particularly in the case of linseed oil, croton oil, and lanolin. The reaction in the estimation of the bromine-substitution number is practically complete after two hours' contact. W. P. S.

Colour Reactions of some Nitro-substances. O. RUDOLPH (*Zeitsch. anal. Chem.*, 1921, **60**, 239—240).—The following colorations are obtained when about 1 milligram of the substance is dissolved in 10 c.c. of alcohol or acetone and then treated with 2 c.c. of dilute sodium hydroxide solution or ammonia :

	Alcohol solution.		Acetone solution.	
	With sodium hydroxide.	With ammonia.	With sodium hydroxide.	With ammonia.
o-Dinitrobenzein	colourless	colourless	colourless	colourless
m-Dinitrobenzene............	,,	,,	intense reddish-violet	pink to purple
p-Dinitrobenzene	,,	no characteristic colour	intense yellow	yellow
1 : 3 : 5-Trinitrobenzene ...	yellowish-red	yellowish-red	blood-red	blood-red
2 : 4-Dinitrotoluene	deep blue	colourless	deep blue	colourless
2 : 6-Dinitrotoluene	colourless	,,	faint pink	,,
2 : 4 : 6-Trinitrotoluene ...	deep yellowish-red	bright red	purplish-red	light red
1 : 8-Dinitronaphthalein ...	yellowish-red	red	yellowish-red	red

W. P. S.

Assay of Aconitine. A. R. L. DOHME (*Amer. J. Pharm.*, 1921, **93**, 426—429).—A physiological method is described and recommended for the valuation of aconite and its preparations, since the ordinary chemical method of extracting the total alkaloids does not differentiate between the amount of aconitine, benzoylaconine, and aconine present, and there appears to be no method available for their separation. Aconitine is about three hundred times as toxic as benzoylaconine and four thousand times as toxic as aconine. In the case of the fluid extract, 1 c.c. is diluted to 10 c.c. with 50% alcohol, and small quantities of this solution, diluted to a volume of 1·5 c.c. with normal saline solution are injected into the subcutaneous tissues of the abdomens of guinea-pigs of about 350 grams body weight. The lethal dose is taken to be the smallest quantity which will kill within twenty-four hours. Approximately 0·00000005 gram per gram of guinea-pig is the lethal dose of aconitine. W. P. S.

Colorimetric Estimation of Carnosine. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1921, **15**, 400—407).—A modification of Koessler and Hanke's colorimetric method for estimating iminazole derivatives (A., 1920, ii, 67). The minced tissue is extracted with a known volume of water at 60—90°. The aqueous extract is then treated with metaphosphoric acid and filtered. An aliquot portion of the filtrate is neutralised to litmus and the depth of colour produced on admixture with sodium carbonate and *p*-diazobenzenesulphonic acid determined colorimetrically in a Duboscq colorimeter. Parallel estimations agree to 0·05 mm. S. S. Z.

Estimation of Acetanilide. A. RECLAIRE (*Perf. Ess. Oil Rec.*, 1921, **12**, 280).—A method, sufficiently accurate for technical purposes, for the estimation of acetanilide, particularly for acetanilide used as an adulterant in artificial musk preparations, is carried

out as follows: About 1·5 grams of the substance are boiled in an acetylation flask with 50 c.c. of 20% hydrochloric acid for fifteen minutes. The volume is then made up to 500 c.c., and to 25 c.c. an excess of a standard potassium bromide–bromate solution and 5 c.c. of strong hydrochloric acid are added. Tribromoaniline is precipitated and the excess of bromine estimated by potassium iodide and sodium thiosulphate in the usual way. One c.c. of *N*/10-thiosulphate equals 0·00225 gram of acetanilide. G. F. M.

A Colour Reaction for Carbamide. VICTOR ARREGUINE and EDUARDO D. GARCÍA (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 183—191).—The colour reactions for carbamide are discussed. The reaction proposed by the authors consists in adding resorcinol and hydrochloric acid to an aqueous solution of the substance under examination and boiling for about one minute. After cooling and dilution with water, the liquid is shaken with ether. The ethereal layer is coloured pink to red, according to the amount of carbamide present. Further colour changes in the ethereal layer are observed on addition of ammonia solution. One milligram of carbamide may be detected by this test, which is also given to a less degree by guanidine and substances giving carbamide under the conditions of experiment. The reaction would appear to be characteristic for the group $=C(NH_2)_2$. It is not applicable to the quantitative estimation of carbamide. G. W. R.

Gasometric Estimation of Urea in Urine. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1921, **47**, 13—17).—The hypobromite method gives results which agree with those obtained by the urease method (A., 1914, ii, 822) if the estimation is carried out in a vacuum after the removal of ammonium salts by means of permutite (cf. Youngburg, this vol., ii, 358). E. S.

Estimation of Urea, Ammonia, and Amino-acids in Urine after Precipitation of the Ammonia. PHILIBERT (*J. Pharm. Chim.*, 1921, [vii], **24**, 49—58. See also A., 1919, ii, 374).—Ammonia is precipitated as ammonium magnesium phosphate and separated by filtration; the filtrate is then treated with basic lead acetate, again filtered, and the urea estimated by the hypobromite method. Another portion of the urine, after the ammonia has been removed, is neutralised towards phenolphthalein, formaldehyde solution is added, and the mixture titrated with standard alkali solution. The results obtained are expressed in terms of nitrogen or of ammonia. W. P. S.

Estimation of Dicyanodiamide and Urea in Fertilisers. ERLING JOHNSON (*J. Ind. Eng. Chem.*, 1921, **13**, 533—535).—A volumetric method proposed for the estimation of dicyanodiamide depends on the formation of the complex silver picrate dicyanoguanidine. Five grams of the sample are shaken for three hours with 450 c.c. of water and 5 c.c. of acetic acid, the mixture is then diluted to 500 c.c., filtered, and 100 c.c. of the filtrate are treated

with 5 c.c. of 20% nitric acid and 20 c.c. of sodium picrate solution (7·5 grams of picric acid neutralised with sodium carbonate and diluted to 100 c.c.; this solution is used at 40° to prevent crystallisation of the salt). The mixture is then cooled in ice-water and a slight excess of silver nitrate solution (7·582 grams per litre) is added and, after fifteen minutes, the whole is diluted to 200 c.c. and filtered. Five c.c. of 20% nitric acid and 2 c.c. of 5% ferric sulphate solution are added to 100 c.c. of the filtrate and the excess of silver is titrated with standardised thiocyanate solution. Each 1 c.c. of the silver nitrate solution is equivalent to 1% of dicyanodiamide-nitrogen. The estimation of urea is based on the formation of urea oxalate; 5 grams of the sample are shaken with 100 c.c. of amyl alcohol, the solution is filtered, 50 c.c. of the filtrate are mixed with an equal volume of ether, and the urea is precipitated by the addition of 25 c.c. of a 10% solution of anhydrous oxalic acid in amyl alcohol. After thirty minutes, the precipitate is collected on a filter, washed twice with a mixture of equal volumes of amyl alcohol and ether, once with ether alone, dried under reduced pressure, and weighed. The precipitate contains 57·01% of urea.

W. P. S.

Reaction for the Micro-chemical Detection of "Chinosol" or 8-Hydroxyquinoline Salts. C. GRIEBEL (*Pharm. Zentr.-h.*, 1921, **62**, 452—456).—A 2% solution of "chinosol" (8-hydroxyquinoline sulphate), when treated with a drop of potassium ferrocyanide solution, yields a bright green, crystalline precipitate, the colour changing within a few minutes to orange-red. The precipitate is formed more slowly from dilute solutions, and is not given when the concentration of the solution is less than 0·5%. With potassium ferricyanide, 8-hydroxyquinoline sulphate solution yields a yellow, crystalline precipitate. W. P. S.

Estimation of Pyramidone (4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone) in Presence of Antipyrine (1-Phenyl-2 : 3-dimethyl-5-pyrazolone) and Aspirin (*o*-Acetoxybenzoic Acid). E. OLIVERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1921, **51**, i, 324—328).—Pyramidone may be estimated in presence of antipyrine and aspirin by taking advantage of the fact that the former, but not the latter, yields dimethylamine when boiled with concentrated potassium hydroxide solution (1 : 1); the amine is collected in a known volume of standard acid and its amount determined by titration: 1 gram of pyramidone is found to correspond with 8·50 c.c. of seminormal sulphuric acid, the theoretical number being 8·64 c.c.

When titrated with seminormal hydrochloric acid in presence of methyl-orange, 2 grams of pyramidone correspond with 16 c.c. of the acid and 0·9 gram of aspirin with 1 c.c. of the acid. Hence, the percentage (A) of aspirin in a mixture of the two compounds is given by the formula $A=9(16{\cdot}6-x)$, where x denotes the number of c.c. of the seminormal acid required to neutralise 2 grams of the

mixture; then $100-A$ gives the percentage of pyramidone. [See, further, *J. Soc. Chem. Ind.*, 1921, 600A.] T. H. P.

Estimation of Veronal in Urine and Human Organs. L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1921, **58**, 1062—1068).—Ethyl acetate is preferable to ethyl ether for extracting veronal from urine, the solubility being 1 : 8·9 in the former, and 1 : 18·7 in the latter. When the extract is purified with charcoal, low yields are obtained owing to adsorption. Treatment of the urine with lead acetate or basic lead acetate effects precipitation of some of its constituents and prevents emulsification during the extraction; by treatment of the extract with potassium permanganate, a quantitative yield of pure veronal is obtained. The method is as follows: 100 c.c. of urine are treated with 10 c.c. of lead acetate (or basic lead acetate) solution, and filtered. The filtrate is evaporated to 25 c.c. and acidified with acetic acid. It is then extracted with twice its volume of ethyl acetate, filtered, and evaporated; the residue is dissolved in 10 c.c. of boiling water, with addition of 5 c.c. of dilute sulphuric acid, and $N/10$-potassium permanganate solution added until the supernatant liquid is colourless. The manganese oxide formed is decomposed with a few drops of hydrogen peroxide, the liquid is shaken with twice its volume of ethyl acetate, filtered, evaporated, and the residue dried at 100°. With suitable modification this method is applicable also to the estimation of veronal in various organs. W. J. W.

The Colorimetric Estimation of Tyrosine and the Phenolic Number of Proteins. PIERRE THOMAS (*Bull. Soc. Chim. Biol.*, 1921, **3**, 197—216).—In the estimation of tyrosine in proteins by the colorimetric method of Folin and Denis (A., 1912, ii, 1012) the presence of tryptophan, scatole, indole, and reducing reagents vitiates the results; hence the method is untrustworthy and must be rejected (compare Abderhalden and Fuchs, A., 1913, i, 409; Folin and Denis, A., 1913, i, 915). The author suggests the characterisation of proteins by means of their phenolic numbers, the latter being defined as the numbers, calculated in percentages of tyrosine, which represent the phenolic constituents of the hydrolysates. For the estimation of the phenolic number a weighed portion of the protein is hydrolysed with 25% sulphuric acid, filtered from humin, neutralised with barium hydroxide, acidified with nitric acid, and filtered. Just sufficient mercuric nitrate is then added to an aliquot part of the filtrate to precipitate the tryptophan. After decolorisation, if necessary, by addition of a small quantity of animal charcoal, the colour produced by the addition of 2 c.c. of Millon's reagent to 10 c.c. of the filtered solution is compared with a tyrosine standard. The results of a number of estimations are given. E. S.

Some Corollaries of the Laws of Hydrolysis by Enzymes. H. COLIN (*Bull. Soc. Chim. Biol.*, 1921, **3**, 263—272).—Deductions are made from the laws which govern hydrolysis by enzymes and

are illustrated by examples of the hydrolysis of various sugars. The author is able to detect the presence of sucrose in specimens of other sugars, to obtain a quantitative idea of the amount of enzyme present in a given preparation, and to determine the relative molecular weights of various sugars which are hydrolysed by the same enzyme. C. R. H.

A Colour Reaction Common to Antiscorbutic Extracts and to Quinol. N. BEZSSONOFF (*Compt. rend.*, 1921, **173**, 466—468).—A modified form of the Folin-Denis phenol reagent, prepared by adding its own volume of *N*-sulphuric acid to a solution containing 100 grams of sodium tungstate, 20 grams of phosphomolybdic acid, and 16·6 c.c. of concentrated phosphoric acid per litre, is found to give a blue coloration with plant extracts known to possess antiscorbutic properties and no colour, or at least not a blue colour, with extracts devoid of such properties. It is possible that the action is not due to the antiscorbutic substance itself, but to some polyphenol easily detached from it in solution. Of the numerous phenols examined, quinol was the only one to give the blue colour with this reagent.

When evaporated at 40°, the reagent gave monoclinic crystals having the composition $17WO_3,MoO_3,P_2O_5,H_2O,21H_2O$. W. G.

Methods for Estimating the Amount of Colloidal Material in Soils. CHARLES J. MOORE, WILLIAM H. FRY, and HOWARD E. MIDDLETON (*J. Ind. Eng. Chem.*, 1921, **13**, 527—530).—Soil was shaken with water, allowed to settle for twenty-four hours, the turbid liquid then decanted, submitted to centrifugal action, and the resulting opalescent liquid filtered through Pasteur-Chamberlain filter tubes. The colloidal substance collected on the tubes was washed and dried at 110°; it consisted essentially of hydrated aluminium silicate and has been named "ultra-clay." Each 1 c.c. of the ultra-clay absorbed 93 c.c. of dry ammonia gas, but lost this property when heated previously at 1130°. A sample of the soil from which the ultra-clay was obtained absorbed 27·7 c.c. of ammonia per 1 c.c., and 1·4 c.c. of ammonia after previous heating at 1130° (this absorption was probably due to substances other than "ultra-clay") and it is therefore calculated that the soil contained 28·3% of colloidal substance. An exactly similar result was obtained by a method depending on the absorption of malachite green from an ammonium oxalate solution. W. P. S.

General and Physical Chemistry.

The Luminosity of Mercury Vapour Distilled from the Arc in a Vacuum. NORMAN H. RICKER (*Physical Rev.*, 1921, **17**, 195—226).—Considerable evidence is offered in support of Child's contention (*Phil. Mag.*, 1913, [vi], **26**, 906) that the afterglow in mercury distilled from an arc is due to a recombination of positive and negative ions. Strutt's work (*Proc. Roy. Soc.*, 1918, **94**, [*A*], 88) was repeated and confirmed and it is shown to be not inconsistent with Child's conclusion (cf. *Phil. Mag.*, 1919, [vi], **37**, 61). The author obtained enhanced luminosity by heating the mercury cathode. The luminous vapour passed through a hollow nickel anode into a heated tube containing two or more grids. On charging one of the grids positively, a current flow as great as 1 ampere at 5 volts could be obtained. The red glow which first filled the tube diminished on both sides of the grid up to a grid voltage of 2, after which it was replaced by a blue glow. The change in colour was found to be caused merely by a relative change in intensity of certain lines in the mercury spectrum. On charging a grid negatively, the luminosity upstream is not diminished even at 300 volts and downstream but slightly. The current is a small part of an ampere and never reaches saturation; so that quenching is far from complete. A jet of mercury vapour sent into the luminous stream serves merely to dilute the light. The vapour velocity was determined by applying a high-frequency voltage to one grid with a stroboscopic wheel so that the luminosity appeared in puffs which could be accurately observed. The velocity was 3740 cm. per sec. Then from the rate of distillation the vapour density was calculated and shown to be essentially constant along the tube. The rate of decay of luminosity was observed with a Nutting polarisation photometer and compared with formulæ derived on three assumptions: (1) that the positive ions emit light spontaneously and not continuously; (2) that the light is produced during recombination of positive and negative ions, and (3) that light is continuously emitted by positive ions. Formula 2 fitted the observed decay better than 1, each having but one arbitrary constant; but formula 3 with two arbitrary constants would fit almost any set of data; so it is impossible to decide in its case. All the facts observed support Child's claim that the light is caused by recombination of ions. CHEMICAL ABSTRACTS.

Vacuum Spark Spectra in the Extreme Ultra-violet of Carbon, Iron, and Nickel. R. A. MILLIKAN, I. S. BOWEN, and R. A. SAWYER (*Astrophys. J.*, 1921, **53**, 150—160; cf. this vol., ii, 3, 363).—By using a specially ruled grating containing 500 to 1100 lines per mm., the intensities and wave-lengths ($\pm 0{\cdot}2$ Å.) of 75 lines due to carbon (λ 360—λ 1931), of 200 lines due to iron (λ 271—λ 2153), and of 75 lines due to nickel (λ 731—λ 1860) have been measured. CHEMICAL ABSTRACTS.

Intensity Differences in Furnace and Arc among the Component Series in Band Spectra. ARTHUR S. KING (*Astrophys. J.*, 1921, **53**, 161—164).—Under high dispersion, the A_1 series of lines in the cyanogen band at λ 3883 is enhanced over the A_2 series in the furnace as compared with their behaviour in the arc. Some new doublets appeared in the furnace. The two series appear to belong to different temperature classes and may be expected to differ in other characteristics. The cyanogen band at λ 4216 showed similar differences between furnace and arc. In the Swan band at λ 5165 the triplet series is enhanced in the furnace spectrum with reference to the adjacent doublet series. The bearing of these data on atomic structure is pointed out. CHEMICAL ABSTRACTS.

Obliteration of the Characteristic Spectra of Metals by certain Gases. GEORGE E. GIBSON and W. ALBERT NOYES, jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 1255—1261).—When sodium chloride is melted below a spark gap in oxygen and sparks are passed they are brilliant yellow in colour and show the *D* lines distinctly, but if the oxygen is displaced by chlorine the spark becomes pale blue and only the merest trace of the *D* line can be observed, and it is further noticed that the spark passes with great difficulty. Similar experiments were made with a number of gases using sodium, thallium, and mercury salts and it was found that of thirty-seven gases and vapours examined twenty-three obliterated the characteristic lines of the salts used. An approximate measure of the sparking potential was also obtained by placing a parallel spark gap outside the apparatus and varying this until the spark just failed to pass across it. Vapours of carbon disulphide, sulphur, carbon tetrachloride, sulphur dichloride, arsenic, iodine, stannic chloride, bromine, chlorine, nitrogen dioxide, boron trichloride, phosphorus trichloride, arsenic trichloride, silicon tetrachloride, titanium tetrachloride, arsenious oxide, sulphur trioxide, acetylene, sulphur dioxide, selenium, phosphorus, hydrogen iodide, and ferric chloride obliterate the characteristic spectrum, whilst nitric oxide, carbon monoxide, hydrogen sulphide, oxygen, nitrogen, hydrogen, carbon dioxide, ammonia, mercury, hydrogen chloride, hydrogen bromide, thallous chloride, and mercuric chloride do not affect the spectrum. The gases which exert the obliterating power have also a high sparking potential, and in the main are the gases which, on Lewis's theory of molecular structure, are to be expected to have the power of combining readily with electrons or to dissociate in the spark into gases of this character. The parallelism between high sparking potential and power to obliterate the spectrum lines is explained on the assumption that the molecules of gases which have these two properties unite with free electrons to form ions of larger mass which are incapable of producing further ionisation. J. F. S.

Induction Spectrum of Rubidium. LOUIS DUNOYER (*Compt. rend.*, 1921, **173**, 472—474).—Using the method previously applied to cæsium (this vol., ii, 529), the author has obtained an induction spectrum of rubidium showing 332 lines between λ=2294 and

$\lambda = 5525$. The principal rays and their intensities are tabulated in the original. Most of the intense rays have been found in the spark spectrum by Exner and Haschek, but some of the rays of the spark spectrum do not appear in the induction spectrum.

W. G.

The Rôle of Electrical Actions in the Emission and Appearance of certain Types of Rays in the Spectrum of Magnesium. A. DE GRAMONT and G. A. HEMSALECH (*Compt. rend.*, 1921, **173**, 505—511).—The authors have extended their work on the appearance of spark rays of lead and tin in the electric arc (cf. *ibid.*, 1921, **173**, 278) to the case of magnesium. Details are given of the variation in the lines produced by changing the conditions under which the spark or arc is maintained. The arc was struck between magnesium electrodes under glycerol, petroleum, and water, and sparks were passed in hydrogen, oxygen, coal gas, and nitrogen. The emission of spark rays by the arc, under liquid layers, is independent of the nature and conductivity of the liquid. The emission of these rays is apparently regulated by electrical forces, and their sudden cessation corresponds with a certain critical value of the electrical forces below which their emission cannot be sustained. The remarkable symmetrical broadening of the spark ray, as well as the broadening towards the red of the rays of the Rydberg series during the first phase of the arc, is a manifestation of the Stark effect.

W. G.

Fine Structure of Band Spectra. E. GEHRCKE and L. C. GLASER (*Ann. Physik.*, 1921, [iv], **65**, 605—608).—The structure of the band spectra of magnesium, mercury, and carbon has been investigated. As source of light, the arcs of the substances in a vacuum were used. The light from the arc fell on a plane parallel plate 5 mm. thick, and the interference bands, in the same manner as employed by Galli and Förstling (*Physikal. Zeitsch.*, 1917, **18**, 155) were projected on the slit of a prism spectrograph. In the case of magnesium, the lines $\lambda\lambda$ 5529 and 4703 were seen very sharply whilst $\lambda\lambda$ 5184, 5173, 5167, and 4352 and the green triplet were found, but these were less sharp. Mercury showed the lines $\lambda\lambda$ 4358, 4348, 4340, 4078, 4047, and three extended series of lines with the limiting line at $\lambda\lambda$ 4396, 4218, and 4017 respectively. Carbon shows the heads of the bands much less sharply than the preceding cases. Interference is, however, shown by the heads of the carbon bands, particularly at $\lambda\lambda$ 4216 and 4197. The distance between two interference maxima corresponds with 0·16 Å.U. in the blue and 0·15 Å.U. in the violet.

J. F. S.

Spectra of Lead Isotopes. T. R. MERTON (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 84—88).—Comparative measurements of the wavelength of the line 4058 Å.U. with ordinary lead and lead from carnotite showed a difference of $0{\cdot}011 \pm 0{\cdot}0008$ A.U. The difference is about two hundred times that expected on Bohr's theory if the

difference is calculated in the same manner as that between the Balmer lines of hydrogen and the enhanced helium lines. J. R. P.

The Variation with Temperature of the Electric-furnace Spectrum of Manganese. ARTHUR S. KING (*Astrophys. J.*, 1921, **53**, 133—143).—The spectrum produced in the tube resistance furnace at 1700°, 2000°, and 2400° was examined from λ 2795 to λ 8200, but no lines were found beyond λ 6500. The relative intensities of the lines in the arc spectrum and in the furnace spectra at the different temperatures are tabulated, and the temperature classification of the lines is given. Some lines were observed at 1560°; the triplet λ 4031 to 4035 was strong and well reversed at this temperature. As with other furnace spectra, the ultra-violet wave-length limit is shorter the higher the temperature. None of Lockyer's enhanced lines occurs in the furnace. The behaviour of various types of lines is given in detail. Of special interest is the triplet at λ 2800, which is always reversed, and the one at λ 4033 the intensity of which depends on the quantity of vapour present. CHEMICAL ABSTRACTS.

Symmetrical Coupled Groups of Lines in the Iron Spectrum. E. GEHRCKE (*Ann. Physik*, 1921, **65**, 640—642).—A theoretical paper in which the author describes a number of regularities in the violet end of the iron spectrum which are visible in the photographs recently published by Glaser (*Ann. Gewerbe u. Bauwesen*, 1921, **88**, 32). It is shown that six groups of lines exist which both with regard to position and intensity of the components are symmetrical about a middle point. These are a group of six lines, with its centre at λ 4221 Å.U., a group of fourteen lines with the centre at λ 4215, a group of six lines with the centre at λ 4193·3, a group of ten lines with the centre at 4195·5, a group of nine lines with the centre at λ 4235, and a group of sixteen lines with the centre at λ 4199·3. These groups are not quite independent of one another, for it is shown that the two extreme components of the first-named group and the left inner component also belong to the second group. Similar coupled symmetrical groups have also been observed in the spectra of tungsten and molybdenum. It is suggested that a Zeeman effect or a Stark effect on account of the magnetic or electric field of the atom itself is responsible for the regularity, which is explicable if one of the twenty-six electrons on the surface of the atom changed its position due to the action of the field. J. F. S.

Influence of Elevated Temperature on the Fluorescence and Absorption Spectra of Iodine Vapour of Constant Density. J. PRINGSHEIM (*Zeitsch. Physik.*, 1921, **5**, 130—138).—The influence of elevated temperatures on the fluorescence and absorption spectra of iodine vapour has been examined. It is shown that whilst the colour change from green to yellow which occurs in the fluorescence of iodine vapour by raising the vapour density is due to an increased absorption in the short wave-length region of the band spectrum, the superficially quite similar change which is observed by simply

raising the temperature is brought about by a decreased primary absorption and consequent reduced fluorescence in the corresponding spectrum region. The heating of iodine vapour at a constant density brings about, not only a displacement of the intensity in the whole absorption spectrum, but also effects an extensive change in the partition of energy of the individual bands.

J. F. S.

Ultra-red Absorption Spectra of Solid Substances in Thin Layers. O. REINKOBER (*Zeitsch. Physik.*, 1921, **5**, 192—197).—The ultra-red absorption spectra of the ammonium haloids have been measured. The method of preparing transparent layers for examination consisted in subliming the substances on to thin plates of transparent material, such as quartz, fluorspar, and rock salt. The spectra have been measured up to wave-lengths of about 8μ. The method is superior to the reflection method, particularly in the greater clearness of the spectra obtained. The following characteristic frequencies have been observed: ammonium fluoride 3·5, 4·5, 5·0, 6·0 ?, and $6{\cdot}69\mu$; ammonium chloride, 3·24, 3·5, 4·25, 4·95, 5·66, and $7{\cdot}07\mu$; ammonium bromide, 3·22, 4·3, 4·9, 5·9, and $7{\cdot}10\mu$; ammonium iodide, 3·22, 4·27, 5·0 ?, 6·0 ?, and $7{\cdot}15\mu$. These values are claimed to be more accurate than the corresponding values found by the reflection method, and they contain twelve values not found by that method. J. F. S.

Absorption Spectrum of Oxygen. J. DUCLAUX and P. JEANTET (*Compt. rend.*, 1921, **173**, 581—583).—Using a water prism, the authors have studied the ultra-violet absorption spectrum of oxygen, between $\lambda=1900$ and 2000. In addition to the seven bands observed by Bloch between $\lambda=1830$ and 1960, they find an eighth belonging to the same group which corresponds with the frequency formula $N=50727-2{\cdot}8m^2$, where $m=1$ to 9. A ninth band was observed but exact measurements were not made. A second group of bands similar to, but much weaker than, the first was observed in this region. The second group may be deduced from the first by a simple translation in the frequency scale, there being a difference of 1555 in the frequencies of corresponding rays in the two groups. W. G.

The Calculation of the Colour of "Cyclic" Coloured Substances. JAMES MOIR (T., 1921, **119**, 1654—1668).

The Numerical Values of the Optical Rotations in the Sugar Acids. P. A. LEVENE (*J. Biol. Chem.*, 1921, **48**, 197—202).—A theoretical paper in which calculations are made, by Hudson's method, of the optical rotations of the different asymmetric carbon atoms in the hexosamic acids. Using different combinations of four equations, it is shown that constant values for the β, γ, and δ carbon atoms are obtained only when the combination is so chosen that the value for the α-carbon atom is the same for each member of the combination. The author concludes that the superposition theory holds only within certain limits. E. S.

The Inversion of the Rotatory Power of Derivatives of Tartaric Acid. D. DE MALLEMANN (*Compt. rend.*, 1921, **173**, 474—477; cf. this vol., i, 158).—Sodium hydrogen *d*-tartrate shows a diminution in its rotatory power when dissolved in a saturated solution of sodium chloride and an inversion when dissolved in a strong solution of calcium chloride. Similarly, calcium *d*-tartrate shows a slight lævorotation when dissolved in calcium chloride solution. Ethyl *d*-tartrate has its rotatory power inverted in the presence of calcium chloride in either aqueous or alcoholic solution. Contrary to the effect of calcium chloride, the presence of copper chloride results in an increase in the rotatory powers of both *d*-tartaric and *d*-malic acids, both acids becoming more dextrorotatory. W. G.

Photochemical Decomposition of Silver Bromide. I. ROBERT SCHWARZ and HEINRICH STOCK (*Ber.*, 1921, **54**, [*B*], 2111—2122).—Owing to the non-availability of a suitable source of artificial light, the experiments deal with the behaviour of silver bromide towards daylight the intensity of which is measured by a self-recording actinometer. The silver bromide is prepared by the slow addition of potassium bromide solution (10%) in moderate excess to a dilute solution of silver nitrate acidified with nitric acid, the solutions being gently mixed; the preparations are effected in red light. The silver bromide is used in three forms (*a*) a caseous, flaky modification prepared as described, which passes when preserved into the plastic variety (*b*), and (*c*) the pulverulent modification obtained by shaking (*b*) with water. The silver bromide is allowed to settle on the bottom of small crystallising dishes in the form of a thin, uniform film and is washed repeatedly with water until free from bromide ions. It is covered with water and exposed to light in an apparatus which is so arranged that a current of air carries the liberated bromine into an aqueous solution of potassium iodide. According to the intensity of the illumination, the production of bromine is noticeable at the end of five to fifteen minutes. The experiments were generally continued for about four hours, at the end of which the bromide had assumed a pale grey to brown colour; variety (*a*) retains its caseous consistency, whereas the more compact form (*b*) suffers a further contraction and sometimes becomes detached from the edges, whilst form (*c*) remains unchanged except with regard to colour. The elimination of bromine occurs with the same regularities as are observed in the blackening of photographic emulsions. The sensitiveness of the various forms towards light diminishes in the order *b*—*a*—*c*. The time which is allowed for the transformation of form *a* into *b* is a matter of considerable importance, since the sensitiveness again diminishes when the form is more than one hundred and ten hours old. The most sensitive products are obtained after eighty to ninety hours. It is probable that a gradual change of form *b* into the less sensitive variety *c* occurs when agitation is avoided. Solarisation is a property of pure silver bromide, and is accompanied by diminished elimination of bromine. Speci-

mens of silver bromide obtained by the action of an excess of silver nitrate on potassium bromide do not evolve bromine when illuminated, but yield, in its place, a volatile substance which oxidises iodine. The phenomenon is explained on the hypothesis that the precipitate adsorbs silver nitrate and that fission of the silver bromide into silver and bromine actually occurs; the latter reacts with the adsorbed silver nitrate with the formation of hypobromous acid; the latter is removed by the air and oxidises the iodine in accordance with the equation: $I_2+5HBrO+H_2O=2HIO_3+5HBr$. The constancy in weight which has been observed in silver bromide when prepared in this manner and subjected to illumination is attributed to the re-formation of silver bromide from hypobromous acid and the liberated silver. Pre-illumination of silver bromide (by cautious exposure to light during precipitation) causes a greatly increased liberation of bromine on subsequent exposure. H. W.

The Developing Properties of Leuco-bases of Dyes derived from Rosaniline. A. LUMIÈRE, L. LUMIÈRE, and A. SEYEWETZ (*Bull. Soc. chim.*, 1921, [iv], **29**, 829—833).—The authors, working with pure substances, were unable to repeat Abribart's results (cf. *ibid.*, 1921, [iv], **29**, 265) on the use of the leuco-bases of malachite green and rosaniline as developers. They consider that his results were probably due to impurities in his leuco-bases. W. G.

The Corpuscular Spectra of the Elements. MAURICE DE BROGLIE and LOUIS DE BROGLIE (*Compt. rend.*, 1921, **173**, 527—529).—A discussion of the results obtained in the corpuscular excitation by X-rays of the heavy metals, uranium, lead, and thorium. The bearing on the L, M, and N layers of electrons is considered. W. G.

Fine Structure of Röntgen Spectra. II. *L* Series. ADOLF SMEKAL (*Zeitsch. Physik.*, 1921, **5**, 91—105; cf. this vol., ii, 292).—It is shown that the whole of the Röntgen lines attributed to the L spectrum of tungsten can be brought into one general scheme, which demands the existence of at least five M layers. The existence of these is rendered fairly certain by a pair of well-defined lines in each case. This number shows the necessity of the determination of the quantum condition of each electron sheath by means of three quantum numbers. The explanation of K_β offered by Kossel (*ibid.*, 1920, i, 119) is confirmed and explanations are given for all hitherto uninterpreted K and L lines, which are in keeping with the relationships as found in the case of tungsten. The new relationships $K_\beta-K_{\beta'}=L_\phi-L_v$ and $K_\beta-K_\alpha=L_\phi+L_1-L_3$ have been tested and found to be in complete accord with the known experimental data within the limits of experimental error.

J. F. S.

Fine Structure of Röntgen Spectra. III. *M* Series and the Principle of Selection. ADOLF SMEKAL (*Zeitsch. Physik.*, 1921, **5**, 121—129; cf. this vol., ii, 292, and preceding abstract).—A paper supplementary to two previous papers (*loc. cit.*) in which

definite frequency relationships are given for the M lines γ and δ, and in the case of the other uninterpreted M lines the most probable of the possible explanations is pointed out. The relationship $M_\gamma = L_3 - L_1 - (L_\phi - L_\gamma)$ is the only relationship giving complete agreement with facts, which can be found from the investigation of a great range of order numbers. It is shown how apparent difficulties in the principle of selection, as in the case of Kossel's arrangement of K_β, may be avoided. On the other hand, on account of a lack of exact relative intensity data for the whole of the lines, it is not possible to draw general conclusions as to the form of the principle of selection which holds for energy levels which are unlike hydrogen. J. F. S.

Action of Infra-red Rays on Phosphorescence. MAURICE CURIE (*Compt. rend.*, 1921, **173**, 554—555; cf. this vol., ii, 233).—No diminution was noticed in the intensity of the radiation reflected from the face 110 of a cubic crystal of blende illuminated by X-rays after inundating the crystal with infra-red rays. W. G.

The Opening up of Earths Poor in Radium. ERICH EBLER and A. J. VAN RHYN (*Zeitsch. angew. Chem.*, 1921, **34**, 477—480; cf. Ebler and Bender, A., 1915, ii, 128).—A number of uranium minerals, including carnotite and the uranium micas autunite and chalcolite, which are found in a magma of sandstone or decomposed granite, have been examined with the object of discovering a simple method of extracting the radioactive elements from the bulk of the inactive material. In the case of Portuguese uranium micas, more than forty times as much radium was found in the micaceous material, separated mechanically from the ground-mass of siliceous material, as in the latter, but the proportion of radium to uranium in the mica, $1{\cdot}7 \times 10^{-7}$, was less than in the ground-mass, $9{\cdot}8 \times 10^{-7}$, the latter being greater than the theoretical value, $3{\cdot}4 \times 10^{-7}$. This anomaly may be explained on the assumption that part of the radium has been dissolved out of the mica by infiltration, and then partly redeposited in the absorbent siliceous mass, consisting of decomposed granite and containing as much as 94·2% of SiO_2. Experiments with normal granite show that over 60% of the radium present is contained in the mica and hornblende, the rest in the felspar, whilst the quartz is free from radium.

More than 80% of the radium present in these minerals can be obtained in the form of crude sulphate by the following method. The powdered mineral is mixed with about an equal weight of sodium or calcium chloride and calcium carbonate, and heated at the sintering temperature (800—1000°) for five or six hours in a muffle furnace. The cooled mass is powdered and extracted with dilute hydrochloric acid containing sulphuric acid and barium chloride. The sulphate precipitate containing the radioactive material can then be readily washed away from the coarse inactive particles and filtered off. The weight of crude sulphates obtained is about 7% of the original ore. This method was used to extract radium from Portuguese torbernite ore containing only $4{\cdot}5 \times 10^{-7}$%,

from Colorado carnotite sandstone containing $5 \cdot 0 \times 10^{-7}$% and from Mexican pitchblende-quartzite containing $2 \cdot 84 \times 10^{-7}$% of radium.

E. H. R.

The Disintegration Constant of Radium Emanation. W. BOTHE and G. LECHNER (*Zeitsch. Physik.*, 1921, **5**, 335—340).—The disintegration constant of radium emanation has been determined by comparing the emanation directly with the radium preparation from which the standard solution was made. Two values of λ were obtained which agreed to one per thousand, and gave a mean of $0 \cdot 1819$ day^{-1}=$2 \cdot 106 \times 10^{-6}$ sec.$^{-1}$. From this the half life is 3·810 days. These values are about 1% greater than the generally accepted Curie-Rutherford values. It is shown that in emanation measurements the often untrustworthy standard solution can be dispensed with if a radium standard and some radium emanation are available. The once determined sensitiveness of the emanation electrometer, found by means of a tube of emanation, may be made the basis of measurements for a long time, if the γ-ray sensitiveness is controlled for each measurement. A table is appended to the paper which gives the decay of radium emanation and the formation in radium preparations which are not in equilibrium.

J. F. S.

Range and Ionisation of the α-Particles from Radium-*C* and Thorium-*C*. G. H. HENDERSON (*Phil. Mag.*, 1921, [vi], **42**, 538—551).—The ionisation curves of Ra-C, Th-C_1 and Th-C_2 in air were measured, particular attention being directed to the end-portions. A considerable part of each curve is approximately a straight line. The gradual flattening of the curve at the end of the range can be accounted for by small variations in the ranges of individual α-particles, due to probability variation in the number of electrons encountered by the α-particle along its path. An "extrapolated range" is suggested as more suitable than the usual definition, and is obtained by prolonging the straight part of the curve. This extrapolated range in air at 0° is 6·592 cm. for Ra-C, 4·529 cm. for Th-C_1, and 8·167 cm. for Th-C_2. A general equation for the end part of the curve is suggested.

J. R. P.

The Accumulation of Radioactive Substance in Ferruginous Spring Deposits. F. HENRICH (*Ber.*, 1921, **54**, [*B*], 1715—1722). The preliminary treatment of the sediment is effected with hydrochloric acid, whereby a portion remains undissolved which contains silica (46·7%), calcium oxide (12·1%), iron oxide (11·5%), aluminium oxide (4·44%) organic matter (3%), and smaller amounts of arsenic, manganese, etc. The solution is treated with ammonia, giving a precipitate containing iron oxide (61%), calcium oxide (5·8%), manganese oxide (5·7%), aluminium oxide (3·67%), and small amounts of arsenic, strontium, etc., together with 2·54% of matter insoluble in hydrochloric acid. The latter is re-dissolved, but enrichment of the solution in radioactive matter is found impossible by fractional precipitation of the iron as ferric hydroxide. If, however, the iron is reduced to the ferrous state and slow

crystallisation of ferrous sulphate is induced, it is found that the initial deposits are completely inactive and the subsequent ones only slightly active, becoming, in general, completely inactive after a single crystallisation from water. A very considerable enrichment of the solution can thus be effected, and the active material can then be deposited on ferric hydroxide by oxidation and subsequent addition of ammonia to the solution. If desired, the last traces of iron can be removed electrolytically from the solution and the active substance then deposited on any desired carrier, but the procedure does not appear to offer any particular advantage.

The residue (see above) is treated with hydrofluoric and sulphuric acids for the removal of silica, whereby the organic matter becomes charred and the carbon disseminated through the inorganic matrix. The latter may be almost completely removed by treatment with boiling hydrochloric acid (1 : 2). The residue invariably exhibits relatively great activity, which is yet more pronounced in the ash left after ignition. Attempts to secure an active deposit by treatment of the solutions with animal charcoal were, however, unsuccessful. The filtrate from the treatment of the charred product is concentrated when gypsum and alum successively separate in an inactive condition; subsequent concentration of the active matter is then effected by the ferrous sulphate method. H. W.

Further Light on the Theory of the Conductivity of Solutions. GUY CLINTON (Pamphlet, pp. 15).—A theoretical discussion of the hypothesis of electrical conduction of solutions. It is pointed out that Kohlrausch's principle is stated first as a law of moving ions and secondly as a function of the resistance. The illustration put forward by Hittorf is examined, and shown to be incapable of showing the possibility of the equivalency of discharge when the ions move with unequal velocity. The same question is examined mathematically, and the conclusion is drawn that Kohlrausch's law of ionic movements is not in harmony with Faraday's law of discharge. It is suggested that the Kohlrausch statements need revision, to keep them within the limit of experimental evidence. The author proposes the following: During the early period of electrolysis, in parts of the cell remote from the points of discharge, with certain amendatory assumptions, the sum of the velocities of the kation and anion is proportional to the molecular conductivity of the solution. It is pointed out that velocities have been measured in but a small part of the cell, whilst resistance is measured for the whole cell, and that such values are not comparable. The author describes a cell in which the velocity for the whole distance between the electrodes is determined. This, only, is comparable with the fall in the potential for the entire cell. It is shown experimentally that the lead ion moves downward toward the cathode with a velocity of 0·113 cm. per sec., but upward to the cathode with a velocity 0·00457 cm. per sec, the potential gradient being unity in each case. Whetham's explanation for the exceptional congestion in solutions of cadmium iodide is quoted, and it is suggested that it might be applied to explain all cases of

congestion. The effect of hydration of ions on ionic velocities is examined. It is pointed out that previous work takes no account of the eddies formed in the system. J. F. S.

Ionic Mobilities, Ionic Conductivities, and the Effect of Viscosity on the Conductivity of certain Salts. DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1921, **43**, 1217—1226).—A theoretical paper in which it is shown that the changes in the transport numbers with concentration indicate that variations of ionic mobility with concentration must be considered in any theory of strong electrolytes. Since the changes in the transport numbers can indicate only differences of mobilities, it seems very probable that the actual changes are greater than these differences. Since there is at present no method of distinguishing between variations of the equivalent conductivity due to (*a*) changes of the number of ions, (*b*) changes of the mobilities of the ions, it seems desirable to consider a group of these substances as completely dissociated, and all variations of conductivity as due to changes of mobility. The latter changes can conceivably arise from the increasing strength with concentration of the electrical field due to the ions. The evidence in favour of this view is most clear in the case of the alkali haloids and hydrochloric and nitric acids. These substances fulfil a further condition of complete dissociation, namely, additivity at each concentration, of the conductivity except in so far as this property is modified by the changing viscosity. Any degree of dissociation less than that represented by the limiting case can be found in solutions of electrolytes, particularly of weak electrolytes and those possessing multivalent ions. But this dissociation cannot be calculated from the ratio Λ/Λ_0, since the changes of the transport numbers with concentration indicate that changes of ionic mobility also occur in these solutions. In the case of strong electrolytes, there does not appear to be any property which can be computed from the conductivity ratio. The activity coefficients of the ions of the alkali chlorides and hydrochloric acid are first lower and then much higher than the corresponding ratios as the concentrations are increased, whilst the free energy contents of these ions have been found to be additive at each concentration, as would be expected if they were completely or almost completely dissociated. J. F. S.

Electrode Reactions. Contractometric Observations at Anodes. V. KOHLSCHÜTTER and H. STÄGER (*Helv. Chim. Acta*, 1921, **4**, 821—837).—An extension of the contractometric method (A., 1920, ii, 728) to the study of anode changes in electrolytically unchangeable electrolytes, yielding hydrogen at a platinum black electrode. The anodes consisted of electrolytic deposits of the metal to be investigated on platinum contractometer plates, a sheet of the metal itself being alternatively employed in the case of copper (cf. A., 1920, ii, 624). The results of a study of platinum anodes in sulphuric acid or sodium hydroxide solution, of nickel, copper, and iron anodes in sodium hydroxide solutions, of passive iron in nitric acid, and of copper and silver in sodium sulphide

solutions show that the method is not inferior in applicability to the dilatometric method. The details do not lend themselves to concise reproduction. J. K.

Electrode Processes in the Presence of Colloids. N. Isgarischev (*Koll. Chem. Beihefte*, 1921, **14**, 25—62).—The cathodic and anodic polarisation in the electrolysis of solutions of zinc sulphate and copper sulphate has been investigated in the presence of gelatin, gum, and sucrose. The potential of zinc and copper has been determined in the same solutions and also the viscosity and the electrical conductivity of the solutions. It is shown that a maximum polarisation is set up and also a maximum potential at a definite concentration of the added substance. In a molecular solution of zinc sulphate the maximum occurs with 0·025% of gelatin, 2% of gum arabic, and 30% of sucrose, and with copper sulphate solution the maximum occurs with 0·30% of gelatin. This maximum is explained by the hypothesis that the kations form adsorption compounds with the colloid and these exert an action on the velocity of the cathode processes, but none on the anode processes. In the case of sucrose, the polarisation is explained as due to a chemical combination between the sugar and the zinc sulphate. The heat of formation of the adsorption compound between the zinc ion and gelatin is found by the electrometric method to be $\Delta Q = -2150$ Cal. The ultramicroscopic investigation of the above-named solutions shows a characteristic change in the form of the particles with increasing colloid concentration. A connexion between the polarisation phenomena and the structure of the electrolytically deposited metals is established. The change in the crystallisation phenomena, the crystalline form of the metal, and the polarisation are brought about by the relatively slow formation of the ions from the complexes. Similar results have also been obtained with solutions of nickel sulphate. In this case the maximum polarisation is found with solutions containing 0·95% of gelatin. J. F. S.

Electrolytic Oxidation and Reduction in Presence of Metallic Salts. Max Schlötter (*Zeitsch. Elektrochem.*, 1921, **27**, 394—402).—In the electrolysis of chloride solutions for the manufacture of chlorate, the addition of a small quantity of a metallic salt, for instance a manganese salt or a chromate, has a favourable effect on the current efficiency of the process, apparently by preventing reduction from taking place in the cell. Experiments to investigate the part played by the metallic salt were made, using as electrolyte a saturated solution of potassium chloride with platinum electrodes. The amounts of reduction and of decomposition of water taking place were determined by analysis of the electrode gases for hydrogen and oxygen. It was found that the effect of the addition of a metallic salt to the electrolyte was determined, not only by the character of the metal, but equally by its concentration. Certain metals, such as copper (0·5 gram of cupric chloride per litre) and lead (0·21 gram lead dioxide per litre), eliminated reduction almost entirely. Tin, when 0·5

gram of stannous chloride per litre was added, had little effect, but when only one-tenth of this quantity was used, reduction was brought down to a very low figure. It was always observed that, after addition of the metal salt, several hours had to elapse before the cell settled down to a steady state. This is probably due to the time required for the deposition of the metal on the electrode. Since the most favourable results are obtained with a very small quantity of added metal, it appears that the cathode does not then become completely covered with the deposited metal, but that the latter forms a network over the electrode metal. The form of electrode which then gives the best results is probably one which consists of the system electrode metal–deposited metal–hydrogen. This conclusion was supported by experiments in which metals other than platinum were used for the cathode. When a copper cathode is used, addition of copper to the electrolyte has no effect on the reduction. With an iron electrode addition of copper increases the amount of reduction in the cell, whilst with a copper electrode addition of iron lowers the percentage reduction, although the reduction value of a pure iron electrode is much higher than that of a pure copper electrode. This is explained by the fact that electrolytically deposited iron absorbs more than one hundred times its volume of hydrogen, forming a stable system in which the activity of the hydrogen is reduced to a low value. The potential energy of the hydrogen at the cathode depends on the nature of the deposited metal, and it should be possible, by choosing a suitable system, to obtain conditions for the quantitative reduction of any substance. E. H. R.

Velocity of Sound in Gases at High Temperatures and the Ratio of the Specific Heats. HAROLD B. DIXON, COLIN CAMPBELL, and A. PARKER (*Proc. Roy. Soc.*, 1921, [*A*], **103**, 1—26).—Direct measurements were made of the time taken by a sound wave to travel through the gas contained in a tube of known length, by means of a pendulum chronograph. The sound was propagated through tubes of lead, mild steel, and silica. The lead tubes were used up to 100°; at higher temperatures, the steel and silica tubes were used, being heated in a gas furnace, and electrically, respectively. The values of c_p/c_v, and the true specific heats calculated by Berthelot's equation, are given: for air (0—700°), nitrogen (0—1000°), carbon dioxide (0—600°), methane (0—600°), and ethane (0—100°), and the values of c_v are represented by the following equations (t=temperature; T=absolute temperature): nitrogen $4{\cdot}775+0{\cdot}00042T$; air $4{\cdot}8+0{\cdot}0004T$; carbon dioxide $6{\cdot}30+0{\cdot}00205T+0{\cdot}0000007T^2$; methane $6{\cdot}66+0{\cdot}019t$; ethane $9{\cdot}04+0{\cdot}0183t$. J. R. P.

Ratio of the Specific Heats of Air and Carbon Dioxide. J. R. PARTINGTON (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 27—49).—The values of c_p/c_v for air and carbon dioxide at 17° were found by the method of adiabatic expansion and the specific heats calculated by Berthelot's equation. For air, $c_p/c_v=1{\cdot}4034$; for carbon dioxide, $c_p/c_v=1{\cdot}3022$. J. R. P.

Freezing Points of Organic Substances. VI. New Experimental Determinations. J. TIMMERMANS and TH. J. F. MATTAAR (*Bull. Soc. chim. Belg.*, 1921, **30**, 213—219; cf. A., 1911, ii, 854; 1914, ii, 168; this vol., ii, 430—431).—The freezing points of seventy-three compounds of the fatty series, liquid at the ordinary temperature, including alkyl haloids, ethers, ketones, acid anhydrides and chlorides, esters, and amines, are given in tabulated form with notes and references to earlier determinations where such have been made. The freezing points given range from $-13°$ to $-140°$.

J. H. L.

Some Relations between Absolute Critical Temperatures of Ebullition and Fusion. J. J. VAN LAAR (*J. Chim. physique*, 1921, **19**, 4—8).—The regularities described by Prud'homme (A., 1920, ii, 587) are purely arithmetical and have no physical meaning. Relations are deduced from the formula of van der Waals: $\log p/p_c=f(T_c/T-1)$, where f may depend slightly on temperature. If T_1=boiling point, $p=1$ atm., then $\phi_1=T_c/T_1=\log p_c/f_1+1$. ϕ_1 will therefore be approximately constant unless p_c is abnormal (helium). In the case of fusion, $(v_2-b_2)/v_2=1/14$, where v_2-b_2 is the effective volume for molecular motion. Thence $\phi_2=T_c/T_2=2a_c/\gamma a_2$, where T_2=m. p., a is the attraction constant, and γ is usually 0·9, but for ideal substances (a and b constant) is 0·5. For ordinary substances, $a_2=1{\cdot}4a_c$; $\phi_2=2$. For limiting substances (with T_c from 400 to 500°), $\phi_2=1{\cdot}83$, which agrees with the rule of Timmermans (this vol., ii, 430) that the melting points of different families of substances tend to an upper limit of 117° C.

J. R. P.

A Differential Thermometer. ALAN W. C. MENZIES (*Proc. Nat. Acad. Sci.*, 1921, **7**, 81—83).—A water-filled differential thermometer for use in ebullioscopic measurements is described. The thermometer consists of a length (12 cm.) of stout-walled pyrex glass blown to a bulb at its upper end and bent and enlarged at its lower end. Before sealing, all air is expelled by boiling, so that the pressure generated at either end is due to the vapour of the indicating liquid. Both the stem and the lower bulb are graduated in mm. The various errors associated with the Beckmann thermometer are discussed in connexion with the present instrument.

J. F. S.

Applications of a Differential Thermometer in Ebullioscopy. ALAN W. C. MENZIES and SIDNEY L. WRIGHT (*Proc. Nat. Acad. Sci.*, 1921, **7**, 77—80).—The authors described a modification of the Cotterell ebullisocopic apparatus (A., 1919, ii, 447; 1921, ii, 240) which involves the use of a loose pump which is hung on the lower bulb of a differential thermometer (cf. preceding abstract), a sealed-on condenser attached to the top of the boiling tube, and down the centre of which is a glass rod attached to the thermometer to hold it in position. The bottom of the boiling tube is constricted to form a bulb, which contains the whole of the solvent. and a graduated neck. In this way, the volume of liquid may be read immediately

the ebullition has ceased and before the condensed liquid has had time to drain back into the bulb. The apparatus has no corks in its construction. The authors claim that with this apparatus readings may be obtained as rapidly as fresh portions of the dissolved substance can be weighed, and these have an error not larger than 0·5%. J. F. S.

An Improvement in Barger's Method for the Estimation of Molecular Weight. KARL RAST (*Ber.*, 1921, **54**, [*B*], 1979—1987).—The main innovation consists in the replacement of the individual drops used in the original method (T., 1904, **85**, 286) by a single larger drop which is placed in a capillary tube and is fixed at one end. The variations in the size of the drop are therefore much greater and a single reading only is involved. A further advantage lies in the possibility of using volatile solvents such as ether or pentane, whilst, in addition, less trouble is involved when less volatile solvents are used at increased temperatures.

A capillary tube, 0·5—1·2 mm. in external diameter and 20—30 cm. long, is filled successively to a length of about 5 cm. with the comparison solution, a bubble of air 3—4 mm. long, and then with the solution under investigation to a length of 4—5 cm. The latter is drawn into the tube so as to leave about 3 cm. free. The "comparison" end of the tube is sealed and the other end drawn out to an exceedingly fine capillary, which is broken off so that a length of about 2 cm. remains, and is then sealed. The "comparison" end is broken and the solution allowed to flow down to the fine point, after which it also is drawn out and sealed. The tube is now mounted in a Petri dish, and the observations are made under the microscope as in the original method. It is convenient to have the two solutions of different colours; a suitable standard is provided by azobenzene for all solutions which are not red, and by naphthalene for red solutions. Solvents of low boiling point, for example, ethyl ether, ethyl acetate, acetone, carbon disulphide, alcohol (90%), or a mixture of pyridine and acetone, are particularly serviceable, since the changes then occur with convenient rapidity. If desired, a series of solutions, separated from each other by bubbles of air, may be used in the same capillary. H. W.

A Flame with Very High Temperature. ERNST HAUSER and ERNST RIE (*Sitzungsber. K. Akad. Wiss. Wien,* 1920 [IIA], **129**, 539—547; from *Chem. Zentr.*, 1921, iii, 588).—An inflammable liquid is fed to a specially constructed burner, where it is atomised by means of a chemically indifferent gas (hydrogen) to a horizontal cone. This is invested with a mantle of oxygen blown from the peripheral portion of the burner. A temperature of more than 3000° is thus obtained. Using this flame, carbon was changed into graphite or, under certain conditions, into minute, transparent, highly refracting crystals. G. W. R.

Radiation Theory of Thermal Reactions. W. C. M. LEWIS and A. MCKEOWN (*J. Amer. Chem. Soc.*, 1921, **43**, 1288—1306).—A theoretical paper in which an expression is obtained for the

velocity of a unimolecular reaction in a gaseous system, on the basis of the radiation hypothesis of thermal reactions, making use of continuous absorption of radiation by an oscillator. The expression obtained is $k_{\text{uni}}=(8\pi^2e^2n_m{}^3\nu^2/3mc^3)\cdot\epsilon^{-h\nu/kT}$, in which k_{uni} is the unimolecular velocity constant, e and m are the charge and mass of the electron, ν is the frequency of the radiation characteristic of the reaction, k and h are the constants of Boltzmann and Planck, respectively, T is the absolute temperature, and n_m the refractive index of the substance in an ideal state corresponding with the closest possible packing of the molecules. The term n_m is shown to have a value of approximately 200, which is practically independent of the system considered and of the temperature. The expression for the velocity constant agrees with the experimental data of unimolecular reactions, so far as they are known. By considering reversible reactions of the dissociation type, an expression is obtained for the equilibrium constant which is shown to be in good agreement with the experimental data for iodine given by Bodenstein and Starck (A., 1911, ii, 20). Recent criticisms of the radiation hypothesis have been considered and answered. In view of the nature of the criticisms, it is essential to emphasise the distinction rather than the resemblance between thermal and photochemical processes. The resemblance lies in the fact that both processes are attributed to radiation, whilst the distinction enters in the manner and extent to which the transformation of radiant energy occurs. Thus Langmuir attributes the mechanism of a thermal process to rate of emission from a surface, which mechanism, however, characterises photochemical action only. On the other hand, Lindemann considers photochemical action, but regards it from the point of view of radiation density, which is shown to define thermal velocity and not photochemical velocity, when the radiation has the same temperature as the matter. J. F. S.

Volume of Kations in Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. Physik.*, 1921, **5**, 324—330; cf. this vol., ii, 9).—The molecular volume has been determined at 18° for a number of permutites containing different kations, and from the space taken up by the kation the kation volume has been calculated for lithium, sodium, potassium, ammonium, rubidium, silver, magnesium, calcium, strontium, barium, cadmium, thallium, lead, and uranyl ions. These values are compared with the atom radius and the kation radius. In most cases, the determined kation volume is smaller than the atomic volume; only in the case of the four elements with large atomic weights, silver, cadmium, lead, and thallium, is the reverse the case. In the case of lithium, potassium, and rubidium, the atomic radii agree very nearly with those deduced by Lorenz from diffusion experiments in mercury. J. F. S.

Surface Tensions of Salts of the Fatty Acids and their Mixtures. ERIC EVERARD WALKER (T., 1921, **119**, 1521—1537).

Adsorption of Gas by Charcoal, Silica, and other Substances. HENRY BRIGGS (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 88—102).—The adsorptive capacities of charcoal and silica at liquid

air temperatures ($-150°$) were compared, especially as relates to hydrogen and nitrogen. Evaluations were made of the volume of solid matter, the interstitial space between the granules, and the internal gaseous space. The pressure of capillaries is not sufficient to account for adsorption. It is argued that a vitreous solid is a complete atomic linking; activation is considered to be the effect of disrupting the solid polymerides, and the means of accomplishing the partial depolymerisation of charcoal and silica is described.

J. R. P.

Stoicheiometry of Adsorption. II. Adsorption of Potassium and Barium Salts of Various Anions. SVEN ODÉN and E. W. LANGELIUS (*J. Physical Chem.*, 1921, **25**, 385—398; cf. this vol., ii, 438).—The adsorption of the hydroxide, bromide, thiocyanate, nitrate, and chloride of potassium and barium, and the iodide, sulphite, fluoride, ferrocyanide, citrate, chromate, sulphate, and chlorate of potassium by charcoal has been determined by the interferometric method previously described (*loc. cit.*). In the case of the potassium salts, the concentration–adsorption curves cross one another, that is, the order of adsorption varies with concentration. With a concentration $0{\cdot}010M$, the order is: fluoride < chloride < sulphate < nitrate < chloride < bromide < ferrocyanide < citrate < chlorate < chromate < iodide, whilst at $0{\cdot}2M$ the order is: sulphate < fluoride < ferrocyanide < chloride < bromide < chromate < citrate < nitrate < chlorate < iodide < cyanide. In the case of the barium salts, the order of adsorption does not change with change in concentration, except perhaps in the case of the acetate, and the order is the same as that for the potassium salts at the concentration $0{\cdot}05M$; the order is: chloride < bromide < acetate < nitrate < thiocyanate < hydroxide.

J. F. S.

Adsorption by Precipitates. IV. HARRY B. WEISER (*J. Physical Chem.*, 1921, **25**, 399—414; cf. A., 1920, ii, 228; 1919, ii, 269).—A number of experiments on the adsorption of oxalate, chromate, and dichromate ions by hydrated ferric oxide are described, and experiments are also described on the quantities of electrolytes required to coagulate a colloid. It is shown that the amount of electrolyte required to coagulate a colloid is influenced by the rate of addition. Since a quantity of electrolyte that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to have become acclimatised, and the phenomenon is termed acclimatisation. This term is a misnomer, since the colloid does not become acclimtised to the presence of the electrolyte in the ordinary sense of the word. The amount of precipitating ion carried down by a colloid is determined by the adsorption of the electrically charged particles during neutralisation and the adsorption of the electrically neutral particles during agglomeration. The adsorption of oxalate, chromate, and dichromate by hydrated colloidal ferric oxide emphasises the importance of adsorption by neutralised particles in

determining the amount of electrolyte carried down by a precipitated colloid. The drop-by-drop addition of an electrolyte to a colloid over a long period is accompanied by fractional precipitation of the colloid and the precipitating ion. The precipitation value is such a concentration of precipitating ion added all at once that sufficient adsorption to cause neutralisation of the colloidal particles can take place promptly. The necessity for using more electrolyte to effect complete precipitation on slow addition arises, not from the adaptability of the colloid to the presence of the electrolyte, but from the fact that the fractional precipitation during slow addition continually removes ions owing to adsorption by the neutralised particles during agglomeration; and this loss must be compensated. The excess of electrolyte required for a given slow rate of addition is determined by (*a*) the extent to which the colloid undergoes fractional precipitation, (*b*) the adsorbing power of the precipitated colloid, and (*c*) the adsorbability of the precipitating ion. The amounts adsorbed at the precipitating concentration of the various ions are not equivalent, as Freundlich assumes. Adsorption of equivalent amounts effects neutralisation of the charged particles, but adsorption during agglomeration varies with the concentration and adsorbability of the ion. Comparable adsorption values cannot be obtained at the precipitation concentration on account of the variability of the latter. J. F. S.

Method of Photographing Transparent Crystals. M. FRANCOIS and CH. LORMAND (*Bull. Soc. chim.*, 1921, [iv], **29**, 792—807).—Full details are given for the photomicrography of transparent crystals. A simple apparatus is described and illustrated, including a method of illuminating the crystals. Instructions are given as to choice of plates, method of development, and a method for calculating the time of exposure. W. G.

Determination of Crystal Structures by Means of *X*-Rays. M. VON LAUE (*Naturwiss.*, 1920, **8**, 968—971; from *Chem. Zentr.*, 1921, iii, 505—506).—A theoretical discussion showing the limitations of the *X*-ray method for the determination of crystal structures. It is pointed out that the lattice image is not a refraction, but an interference, image. Information as to crystal structure is actually obtained by considering the results obtained with rays falling at different angles and of different wave-lengths. Additional information is given by chemical constitution, the dispersive power of the atoms present for the rays used, crystal form, and the mathematical theory of simple and compound space lattices. G. W. R.

The Chemical Reactions of Crystals and their Relation to the Molecular Structure. F. RINNE (*Z. Metallk.*, 1921, **13**, 401—406).—A theoretical paper dealing with the arrangement of the atoms and molecules in crystals and their relation to the symmetry of the crystal. It is shown that the action of reagents on crystals takes place in a symmetrical manner and if carried out slowly results in the development of symmetrical figures on the surface of the crystals which vary according to the relation of the

face attacked to the axes of the crystal. An explanation of this and of the change of crystal form that some minerals undergo on heating is given, based on the space-lattice theory of crystal structure.

A. R. P.

Methods for [Effecting] the Orientation of Crystal Elements. R. BECKER, R. O. HERZOG, W. JANCKE, and M. POLÁNYI (*Zeitsch. Physik*, 1921, **5**, 61—62).—Several methods are described whereby an axial orientation of crystal elements in various types of substances may be produced. 1. A crystalline powder placed in a magnetic field so arranges itself that individual crystalline particles take up positions corresponding with the inductive action. 2. Subjecting crystalline powders and substances like wax and paraffin to high pressures (4000—5000 atms.) brings about a marked regular arrangement of the particles. This is observed in the case of the substances succinic acid, indigotin, and stearic acid. 3. The cold drawing of metals produces an axial symmetry of the elementary crystals of the metals.

J. F. S.

Constitution of Mixed Crystals and the Space Filling of the Atoms. L. VEGARD (*Zeitsch. Physik*, 1921, **5**, 17—26).—A continuation of previous work (A., 1917, ii, 243). In the present paper the structure of mixed crystals of potassium bromide and chloride, potassium and ammonium chloride, and potassium and ammonium sulphate has been examined by means of *X*-ray spectra, using the Debye-Scherrer powder method. The reflection maxima have been photographed for the mixed crystals named above and their components. The results indicate the replacement of one atom by another in mixed crystals is irregular and unordered, so that mixed crystals are to be defined as those substances which are characterised by an unordered atomic substitution. The change of the position of the reflection maxima denotes a change in the molecular volume. The replacement of bromine by chlorine effects a contraction, whilst the replacement of potassium by ammonium effects an expansion of the crystal lattice. The length of the side of the elementary lattice of the mixed crystals of potassium bromide and chloride is given with great accuracy by the formula $a_m = (p-100)/100 \cdot a_{KBr} + p/100 \cdot a_{KCl}$, in which p is the molecular per cent. of the potassium chloride in the mixed crystal and a_m, a_{KCl}, a_{KBr} are respectively the lengths of the sides of the lattices of the mixed crystal, potassium chloride, and potassium bromide. The crystal lattice of ammonium chloride is shown to be a cubic chlorine lattice centred round a similar nitrogen lattice. It is shown that the ammonium radicle takes up more space in the ammonium chloride lattice than in that of the face-centred type. The diameter of the hydrogen atom is calculated from the data obtained for ammonium chloride and bromide and values between 1·58 Å.U. and 1·68 A.U. obtained.

J. F. S.

The Colloid Mill and its Applications. HERMANN PLAUSON (*Zeitsch. angew. Chem.*, 1921, **34**, 469—472; 473—474).—Two types of machine are described, designed for the preparation of

colloidal solutions by mechanical means. The first type, suitable for dispersing typical colloids in a suitable dispersion medium, depends on the hammer-and-anvil principle, whilst the second, which depends on friction, is suitable for the preparation of colloidal solutions of such substances as minerals, dyes, or carbon. It is shown that definite saturated colloidal solutions can be prepared by means of such machines, but that the saturation limit can be raised by the addition of dispersion accelerators or " dispersators," which may be compared in their action with chemical catalysts. Numerous technical applications of the colloid mill are discussed, especially a new application in the viscose artificial silk process. With a suitable dispersion medium, cellulose can be reduced in the colloid mill to the colloidal form, and in this state it reacts with the theoretical quantity of alkali to form alkali cellulose which in turn reacts smoothly with carbon disulphide to give xanthogenate without the formation of any thio-salts as by-products. [Cf. *J. Soc. Chem. Ind.*, 1921, Nov.] E. H. R.

The Hydration of the Fibres of Soap Curd. III. Sorption of Sodium Palmitate. MARY EVELYN LAING (T., 1921, **119**, 1669—1676).

Statistical Mechanics and Chemistry. E. P. ADAMS (*J. Amer. Chem. Soc.*, 1921, **43**, 1251—1254).—A theoretical paper in which the view is advanced that if the laws of chemical dynamics are found to be consistent with the principles of statistical mechanics it is not only unnecessary, but even unjustifiable, to introduce the quantum hypothesis to derive these laws. The author shows that Tolman's criticism (this vol., ii, 99) of Marcelin's attempt (A., 1915, ii, 328) to base a theory of chemical dynamics on the principles of statistical mechanics, is unfounded. The main point of Tolman's criticism is that Marcelin has confused Gibbs's canonical distribution of an ensemble of systems with the Maxwell-Boltzmann distribution. The author shows that the form of the Maxwell-Boltzmann law used by Marcelin may be derived without making any use of the canonical distribution of Gibbs. J. F. S.

A Piezoelectric Method of Measuring Explosion Pressures. DAVID A. KEYS (*Phil. Mag.*, 1921, [vi], **42**, 473—488).—The piezoelectric properties of tourmaline crystals were used in conjunction with a special form of cathode ray oscillograph to record the pressures developed in explosions and the velocity of explosion waves in water. [See *J. Soc. Chem. Ind.*, 1921, 760A.] J. R. P.

Gaseous Combustion at High Pressures. II. The Explosion of Hydrogen–Air and Carbon Monoxide–Air Mixtures. WILLIAM ARTHUR BONE and WILLIAM ARTHUR HAWARD (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 67—84; cf. A., 1915, ii, 684).—The rise of pressure in the explosion of mixtures of hydrogen and air occurs very rapidly, but there is evidence of development of heat for a short period after the attainment of the maximum pressure. The rise of pressure in the explosion of carbon monoxide and air occurs

much more slowly, and cooling is delayed for a long period after the maximum pressure has been reached. The presence of even 1% of hydrogen in the carbon monoxide-air mixture, at the high initial pressures employed, accelerates the rise of pressure on explosion to a high degree. A theory is proposed to account for the different modes of explosion of hydrogen and carbon monoxide.

J. R. P.

The Propagation of Flame in Mixtures of Ethylene and Air. WILLIAM RONALD CHAPMAN (T., 1921, **119**, 1677—1683).

A Periodic Reaction in Homogeneous Solution and its Relation to Catalysis. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1921, **43**, 1262—1267).—The action of hydrogen peroxide both as an oxidising agent and as a reducing agent has been studied in the case of its reaction with iodine. The reactions which occur are (1) $5H_2O_2+I_2=2HIO_3+4H_2O$ and (2) $5H_2O_2+2HIO_3=5O_2+I_2+6H_2O$. It is shown that far more peroxide disappears from the reacting system than can be accounted for by the above equations, consequently the reaction (3) $H_2O_2 \longrightarrow H_2O+\frac{1}{2}O_2$ must also take place and this is catalysed by the iodic acid-iodine couple. Using a mixture containing $0{\cdot}190M$ hydrogen peroxide and $0{\cdot}094M$ potassium iodate, the reaction was carried out at 60° in the presence of varying concentrations of sulphuric acid by measuring the rate of evolution of oxygen. In the case of $0{\cdot}055N$-sulphuric acid, it is found that after an induction period lasting a very short time the reaction takes place rapidly and smoothly; its rate is proportional to the concentration of both hydrogen peroxide and iodate, and is but little affected by the concentration of hydrogen ion above $0{\cdot}2N$. With a concentration of $0{\cdot}110N$-sulphuric acid, after the induction period (seven minutes) the reaction proceeds smoothly, and a faint permanent iodine coloration is observed, but the velocity of evolution of oxygen is much greater than in the case of an acid concentration $0{\cdot}055N$. With acid concentrations intermediate to the foregoing, the velocity of evolution of oxygen is not uniform, but periodic in nature. Taking acid concentrations $0{\cdot}073N$ and $0{\cdot}0916N$ respectively, it is found that the induction period is eighteen and twelve minutes respectively, and then the evolution of oxygen is periodic. The curves representing this show a series of relatively flat portions followed respectively by very steep portions. In the flat regions the colour due to iodine slowly deepens and in the steep regions slowly fades away. With the more dilute acid, the period is between three and three and a half minutes, but with the more concentrated acid the period slowly increases from ten to thirteen minutes. Thus with $0{\cdot}055N$-acid there is no periodicity, with $0{\cdot}070N$-acid there are periods of ten to thirteen minutes, with $0{\cdot}0916N$-acid periods of three to three and a half minutes, and with $0{\cdot}110N$-acid there is pure catalysis and no detectable periodicity. In the last case, however, it is likely that after a very short induction period the reaction consists of a large number of very short periods. This periodicity is taken

as furnishing direct evidence in favour of the intermediate compound hypothesis of catalysis. An experiment carried out at 25° shows that the periods may be made to extend over several days, and when no shaking takes place the oxygen does not leave the solution in bubbles, thus making the reaction strictly homogeneous.

J. F. S.

The Effect of Temperature on Platinum Black and other Finely-divided Metals. ROBERT WRIGHT and ROBERT CHRISTIE SMITH (T., 1921, **119**, 1683—1688).

Adsorption of Gases by Metallic Catalysts. HUGH STOTT TAYLOR and ROBERT MARTIN BURNS (*J. Amer. Chem. Soc.*, 1921, **43**, 1273—1287).—Measurements of the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene by finely-divided nickel, cobalt, iron, copper, palladium, and platinum have been made at various temperatures with the object of finding the relationship this phenomenon bears to catalytic activity, and particularly to the mechanism involved in hydrogenation reactions. It is shown that adsorption by these metals is a specific property quite different in nature from adsorption by inert adsorbents such as charcoal. The extent of the adsorption is shown to be a function of the mode of preparation, and is especially less pronounced the higher the temperature of preparation of the finely-divided metal. The relationship between this fact and the corresponding facts of catalytic behaviour has been pointed out. The adsorption isotherms have been studied in the cases, nickel and hydrogen and copper and carbon monoxide. In both cases, adsorption increases rapidly with increasing partial pressure below 300 mm., and becomes practically independent of pressure above this point. The significance of irreversible adsorptions of gases has been studied, and reasons are suggested for divergences between different catalysts. It is indicated that, in addition to the adsorption factor, it is necessary to consider some other factor in explaining catalytic activity, and it is shown that a combination of the temperature factor with the adsorption factor in catalytic action suggests a possibility of explaining the divergence between the catalytic activities of various metals.

J. F. S.

Catalytic Hydrogenation of Organic Compounds with Common Metals at the Temperature of the Laboratory. The Activity of Nickel Catalysts prepared at Different Temperatures. Influence of Oxygen on the Nickel Catalyst. IV. C. KELBER (*Ber.*, 1921, **54**, [*B*], 1701—1705; cf. A., 1917, ii, 215).—Willstätter and Waldschmidt-Leitz (this vol., ii, 187) have reduced nickel oxide, prepared by ignition of nickel oxalate, to metallic nickel at 350—360°, and describe the product as incapable of accelerating hydrogenation catalytically unless previously primed with air. The author has been unable to confirm their observations. He has further examined the behaviour of metallic nickel obtained by the reduction of basic nickel carbonate at different temperatures, the operation being effected in

the same vessel as is used for the subsequent hydrogenation experiments, thus avoiding any possible complication caused by exposing the product to air. The activity of the catalyst is examined in the case of aqueous solutions of sodium cinnamate. It is found that metallic nickel prepared at 350—360° is but little inferior in activity to that obtained at 300°, and notably superior to that produced at 210°. The material first described becomes completely inactive when shaken with oxygen at 18—20°, but, if treated with hydrogen at 70—80°, it becomes again active at the temperature of the laboratory. The latter phenomenon was not observed by Willstätter and Waldschmidt-Leitz, since they worked at 60°, a temperature at which the catalyst commences to regain activity.

H. W.

The Influencing of the Activity of Catalysts. IV. Oxidative Catalytic Dehydrogenation of Alcohols. II. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1921, **54**, [*B*], 2033—2037; cf. this vol., ii, 393).—Catalytic dehydrogenation by means of copper, quinoline, and nitro-compounds and oxygen leads to the production of aldehydes from primary aliphatic, aromatic, and heterocyclic alcohols and of ketones from secondary alcohols whereas tertiary alcohols remain unchanged. The method is useful in the cases of difficultly volatile or non-volatile alcohols, but has no advantage over the older processes when the more volatile alcohols are used.

Benzhydrol is almost quantitatively transformed into benzophenone when heated with quinoline and nitrobenzene in a current of oxygen; under similar conditions, triphenylcarbinol is unaffected. The yields of acetaldehyde, propaldehyde, and *iso*butaldehyde are 52%, 57%, and 75% respectively, but the volatility of the corresponding alcohol at the temperature necessary for the reaction renders the completion of the change difficult to secure. Fermentation amyl alcohol gives an 80% yield of the corresponding aldehyde. *o*-Chlorobenzyl alcohol (p-*nitrobenzoate*, yellow, monoclinic prisms, m. p. 93—94°), is converted into *o*-chlorobenzaldehyde (yield 86·2%), whereas furfuryl alcohol gives a 74% yield of furfuraldehyde.

Considering the number of factors involved in the reactions, it is not surprising to find considerable fluctuations in the optimal temperature for each change. The lower limit may be considered to lie at 125—130°, at which amyl alcohol is dehydrogenated; benzylhydrol and furfuryl alcohol give satisfactory results at 145°, benzyl alcohol at 165°, and *o*-chlorobenzyl alcohol at 195°; the upper limit of temperature is 180° and 165° in the cases of benzyl alcohol and furfuryl alcohol respectively. H. W.

The Influencing of the Activity of Catalysts. V. Catalytic Reduction of Esters and Aldehydes. KARL W. ROSENMUND, FRITZ ZETZSCHE, and F. HEISE (*Ber.*, 1921, **54**, [*B*], 2038—2042).—It has been shown previously (this vol., ii, 362) that the reduction of benzoyl chloride to benzyl alcohol is complicated by the reductive fission of benzyl benzoate (formed from unchanged benzoyl chloride

and benzyl alcohol) to benzoic acid and toluene, and by the formation of dibenzyl ether. The first-named reaction is shown in the cases of benzyl benzoate and benzhydryl benzoate to take place readily in the presence of xylene and more slowly in the presence of toluene; it is almost completely inhibited by the addition of quinoline. Benzaldehyde is converted by hydrogen in the presence of palladium and xylene mainly into dibenzyl ether, the production of which is hampered whilst that of benzyl alcohol is facilitated by increasing addenda of quinoline; more powerful regulators, such as "sulphured" quinoline, inhibit the formation of dibenzyl ether. Benzyl alcohol is converted into dibenzyl ether by palladium. The reduction of benzoyl chloride may be represented by the scheme: hydrocarbon $\longleftarrow$ ester $\longleftarrow$ benzoyl chloride $\longrightarrow$ aldehyde $\longrightarrow$ alcohol $\longrightarrow$ ether; any particular member of the series may be made the main product of the change by suitably influencing the catalyst.

H. W.

Non-radiating Atoms. (SIR) JOSEPH LARMOR (*Phil. Mag.*, 1921, [vi], **42**, 595).—The conditions under which an orbital system of electrons does not radiate energy unless disturbed are discussed.

J. R. P.

Escapements and Quanta. (SIR) JOSEPH LARMOR (*Phil. Mag.*, 1921, [vi], **42**, 592—594).—An atom is compared with a clock, the outer electron shell being the pendulum, maintained in continuous vibration by the energy of the core imparted through an unknown escapement mechanism, which parcels out quanta.

J. R. P.

An Atomic Model based on Electromagnetic Theory. I. ALBERT C. CREHORE (*Phil. Mag.*, 1921, [vi], **42**, 569—592).—A mathematical paper. It is shown that the force between two neutral atoms each composed of revolving rings of electrons and stationary charges is not zero on the basis of Saha's theory of the forces (*Physical Rev.*, 1919, **13**, 41). There cannot then be an equilibrium velocity for a ring of electrons, and an atom with stationary electrons is indicated. A model of the hydrogen atom consistent with electromagnetic theory consists of two electrons ($-e$) of the shape of oblate spheroids, one on each side of a smaller positive nucleus ($+2e$) of similar shape, the whole rotating about a common axis. The attractions between such atoms would obey the inverse square law.

J. R. P.

Helium and Hydrogen Models. EDWIN C. KEMBLE (*Science*, 1920, **52**, 581—583).—Closely approximating expressions for the energy of the electrons in Langmuir's model of the helium atom (A., 1920, ii, 656; *Science*, 1920, **52**, 433) are derived from the Wilson-Sommerfeld quantum conditions. Numerical evaluations using Langmuir's data do not give the observed ionisation potential of helium.

CHEMICAL ABSTRACTS.

Scattering of Light in Gases. M. BORN and W. GERLACH (*Zeitsch. Physik*, 1921, **5**, 374—375).—A theoretical paper in which

the scattering of light has been calculated on the basis of the hydrogen, oxygen, and nitrogen models of Bohr and Debye. The depolarisation factor deduced from the figures obtained has been compared with the experimental figures found for this factor by Strutt and Gans. The comparison shows that the order of magnitude is the same in both cases, but neither is there a quantitative agreement nor is the sequence the same for the three models. It is therefore shown that the molecule models do not represent the reality. J. F. S.

The Determination of the Valency Scale of Iron, Cobalt, Nickel, Copper, Manganese, Tin, and Tungsten by means of their Water Vapour Equilibria, and of the Dissociation Pressure of the Oxides of these Metals. LOTHAR WÖHLER and O. BALZ (*Zeitsch. Elektrochem.*, 1921, **27**, 406—419).—Experiments were made to determine the true number of oxides of iron by measuring the equilibrium constants when ferric oxide is reduced by a gradually increasing amount of hydrogen, or, conversely, when iron is oxidised by an increasing amount of water vapour. The equilibrium constant was determined by measuring the concentrations C_{H_2O} and C_{H_2} of water vapour and hydrogen respectively in equilibrium with the solid phase. The apparatus used was similar to that previously described by Wöhler and Prager (A., 1917, ii, 455). Only three equilibrium constants were found, corresponding with equilibria Fe_2O_3/Fe_3O_4, Fe_3O_4/FeO, and FeO/Fe, the first being the highest, numerically, and the second the lowest. Since, in the experiments, a known weight of ferric oxide was taken, and known volumes of hydrogen for the reduction, the exact composition of the solid phase could be determined when the value of the equilibrium constant changed. In this way it was shown that the only oxides of iron formed, either by reduction or oxidation, were FeO, Fe_3O_4, and Fe_2O_3. The primary product of oxidation of iron with water vapour at a red heat is FeO, not Fe_3O_4 as has been stated. The values of the equilibrium constants C_{H_2O}/C_{H_2} found were, for Fe_2O_3/Fe_3O_4, 7·5 at 350° to 17·9 at 950°; for Fe_3O_4/FeO, 1·03 at 640° to 5·07 at 950°; for FeO/Fe, 0·62 at 750° to 0·92 at 990°.

The same method was also applied to determining the valency scales of other metals. The highest oxide of cobalt, Co_2O_3 was too unstable for equilibrium determinations. The constants for Co_3O_4/CoO and CoO/Co were determined at 450°, the values being respectively 34·4 and 13·5. No other oxide of cobalt was found. In the case of nickel, the oxide Ni_3O_4 was too unstable for determinations to be made, since it begins to decompose below 450°. The value of the constant for NiO/Ni is about 14·8 at 450°. The so-called nickel sub-oxide is a mixture of NiO and metal. From the fact that Ni_3O_4 is less stable than Co_3O_4 it may be concluded that nickel is nobler than cobalt.

In the case of copper oxides, the following constants were found at 450°: CuO/Cu_2O, 26·3; Cu_2O/Cu, 16·7. In the manganese series the only constant determined was Mn_3O_4/MnO at 450°, 34·6.

Stannous oxide was found to be a stable intermediate stage between tin and stannic oxide, both in oxidation and reduction, the values found being, for SnO_2/SnO, 13·6, and SnO/Sn, 7·9, both at 700°. In the case of tungsten, between tungsten trioxide and the metal, only the bluish-violet W_2O_5 and the brown WO_2 were found as stable phases. The blue oxide with an oxygen value between WO_3 and W_2O_5 is a mixture. The values found were, WO_3/W_2O_5, about 16·0 at 800°; W_2O_5/WO_2, about 5·0 at 800°; WO_2/W, about 1·0 at 950°.

Applying van't Hoff's equation, the heat of reaction for the equation $Fe+H_2O=FeO+H_2$ was calculated from the temperature coefficient of the equilibrium constant, and agreed well with values calculated from other data. In the case of the reaction $3FeO+H_2O=Fe_3O_4+H_2$, the values calculated for the heat of reaction agreed less well, probably because the temperature coefficient of the specific heat of the solid phase introduced an unknown error. The dissociation pressures of the different oxides were also calculated. For the oxides of tin, iron, and tungsten at 1000° these are of the order of 10^{-11} to 10^{-12} mm. of mercury. E. H. R.

New Apparatus for the Generation of Gas. F. HAHN (*Chem. Zeit.*, 1921, **45**, 992).—The numerous forms of apparatus proposed for the generation of gases by the action of liquids on solids are essentially modifications of either Kipp's or Küster's apparatus. Kipp's apparatus has the disadvantage that the acid cannot be completely exhausted, as it is in Küster's apparatus, owing to the mixing of used and fresh acid, whilst Küster's apparatus has the serious disadvantage that, after the gas generated while the apparatus is at rest has been delivered, for some time as much acid must be run in as the volume of the gas delivered, and consequently, when the gas is shut off, the apparatus cannot contain the gas which continues to be generated. These disadvantages are avoided in the new apparatus, which may be of either the Kipp or Küster type. In the former case, the connecting tube from the upper globe is bent slightly to one side and reaches to the bottom of the middle compartment. The middle compartment is connected to the bottom compartment by a tube, the top of which is above the level of the liquid when the apparatus is not in use, and there is a fine orifice somewhat below the upper end of the tube. F. M. R.

Improvements in the Soxhlet Extraction Apparatus. OSKAR HAGEN (*Zeitsch. angew. Chem.*, 1921, **34**, 499—500).—An improved form of the extraction apparatus described previously (this vol., ii, 104). The syphon is done away with, and the condensed solvent dropping from the condenser is not allowed to accumulate in the extraction cylinder, but flows down immediately into the flask after percolating through the material. By this means extraction can be completed in from one-quarter to two-thirds of the time required by the old apparatus. The outlet from the extraction chamber to the flask is bent into a convolution to serve the double purpose of forming a trap to prevent the vapour from the flask rising through the extraction chamber, and, by means of a two-way

tap situated at the top of the loop, to provide a means of withdrawing for testing purposes a sample of the liquid leaving the extraction cylinder. All joints in the apparatus are ground in, as even the best quality corks yield about 10% of their weight in extractive matter to ether. G. F. M.

Inorganic Chemistry.

Some Negative Attempts to Transmute Elements in accordance with Marignac's views on the Unity of Matter. E. BRINER (*J. Chim. physique*, 1921, **19**, 9—10).—The action of an electric arc on iodine vapour and a mixture of helium and hydrogen produced no transmutation, although the temperatures of isolated molecules must have been very high. J. R. P.

Rapid Method for Determining the Density of Air. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1921, **43**, 1317—1318).—A rapid method for determining the density of the air is described. A sealed globe of known exterior volume is weighed under accurately known conditions of temperature, pressure, and humidity. From the conditions, the density of the atmosphere at the time of weighing and the buoyancy effect of the air on the globe and weights may be calculated. By adding the difference between the buoyancy effect on the globe and on the weights to the weight of the globe in air, the weight of the globe in a vacuum is found. If the globe is weighed in the air under any conditions, the weight of air displaced by the globe in excess of that displaced by the weights is readily found by subtraction from the weight in vacuum. This difference divided by the volume of the globe less the volume of the weights yields the atmospheric density. Numerical examples illustrating the method are given in the paper. J. F. S.

Variations of Density of Atmospheric Air. A. JAQUEROD and CH. BOREL (*J. Chim. physique*, 1921, **19**, 11—28).—The variations of density of the air in the region of Neuchâtel follow the Loomis-Morley law. The amplitude of the variations does not usually exceed 0·5—0·6 mg. The same result was found with air taken at 2000—5000 m., but the amplitude is smaller. The explanation which assumes the presence of a heavy gas must be rejected and the presence of ultramicroscopic dust is suggested. J. R. P.

Oxidation of Sulphites in Concentrated Solutions. J. MILBAUER and J. PAZOUREK (*Chem. Listy*, 1921, **15**, 34—38).—Concentrated solutions of sulphites are oxidised slowly but quite constantly at ordinary temperatures by air. (Cf. Lumière and Seywetz, *Rev. gen. chim.*, **7**, 15.) Cobalt sulphate, used in concentrations of 0·01 and 0·001 molar, acts as a positive catalyst for

this reaction. Manganese and copper salts, contrary to results obtained with dilute solutions by Bigelow (A., 1898, ii, 506) and Schilow (A., 1903, ii, 276), are not very active catalysts in concentrated solutions of sulphites. In concentrated solutions 0·5 molar, weak alkalinity of the medium intensifies the oxidation, if no precipitation of the catalysing agent is caused. Strong alkalinity retards the reaction. An acid medium has a similar influence. The rapidity of the reaction increases with rising temperatures.

CHEMICAL ABSTRACTS.

Colloidal Selenium. A. GUTBIER and R. EMSLANDER (*Ber.*, 1921, **54**, [*B*], 1974—1978; cf. Meyer, A., 1913, ii, 1048; Gutbier and Emslander, A., 1914, ii, 264).—Very stable colloidal solutions of selenium may be prepared by the regulated action of concentrated hydrazine hydrate solution on selenium dioxide or gray, crystalline selenium and subsequent dilution of the solutions with water and purification by dialysis. According to the degree of dispersivity, the colour of the solutions varies from intense yellow to blood-red. The dilute solutions are stable at the boiling point, but are readily coagulated by barium sulphate. The action of electrolytes at the atmospheric temperature has been investigated by mixing $2N$-solutions of them with an equal volume of the dialysed system. Hydrochloric, nitric, sulphuric, selenious, and acetic acids immediately change the yellow colour to pink which becomes violet and then blue when the mixtures are gently warmed, thus indicating the formation of coarser aggregates; ammonia has no effect, sodium hydroxide lightens the colour slightly, whereas barium hydroxide causes immediate separation. The coagulating effect of calcium chloride, barium chloride, and alum is particularly marked, whereas that of sodium and potassium chlorides is weaker. Sodium and potassium carbonates appear to increase the stability of the system. The preparations can be frozen to a blue ice, which melts with complete coagulation. With dilute solutions of selenium, on the other hand, the presence of hydrochloric acid, sodium carbonate, or potassium chloride exerts a protective effect in this connexion which is at a maximum at certain definite concentrations; with more concentrated solutions, however, the optimum effect is less definite. H. W.

Tellurium Sub-bromide. A. DAMIENS (*Compt. rend.*, 1921, **173**, 583—586).—Tellurium sub-bromide, $TeBr_2$, has now been isolated in the solid state, either by rapidly cooling its vapour in a dry vacuum to $-80°$ or by reduction of the tetrabromide in dry ethereal solution in the dark with finely-divided tellurium. The sub-bromide so obtained is chocolate-brown in colour and is decomposed by water. It is completely soluble in dry ether, but it is unstable in this solution, readily decomposing to give tellurium and tellurium tetrabromide. In ethereal solution it combines with iodine to give *tellurium iodobromide*, which is completely soluble in ether and crystallises from it in red crystals. W. G.

Oxidation and Luminescence of Phosphorus. II. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1921, **25**, 349—384; cf. this vol., ii, 248).—The various types of emission of phosphorus during oxidation have been considered historically and experimentally from four points of view, (i) emission of gaseous ions, (ii) emission of penetrating radiations, (iii) emission of phosphorus emanation, and (iv) emission of light. It is shown that gaseous ions are formed during the oxidation of phosphorus, and these account for the conductivity of "phosphorised air." These ions furnish nuclei about which oxides and water vapour condense, forming clouds. The cloud arising from glowing phosphorus contains equal numbers of positive and negative particles if the phosphorus is not charged. Ions are formed in the reaction zone and may be withdrawn by an electric field against a current of air sufficiently rapid to remove oxide particles and ozone. The decomposition of ozone and the action of ultra-violet light are unimportant as sources of ions in "phosphorised air." The luminescence of phosphorus is not changed appreciably by charging the element. Radiations of the nature of radium rays, which penetrate black paper and thin metal plates, are not formed during the oxidation of phosphorus. The darkening of a photographic plate protected from light in the region of glowing phosphorus is due to the action of the vapours of hydrogen peroxide and phosphorous oxide. Ions are formed during the oxidation of phosphorous oxide, and render the surrounding atmosphere a conductor. No evidence was obtained of the formation of phosphorus emanation by the action of moisture on phosphorous oxide. The vapours of phosphorous oxide diffuse readily and when admitted to an electrometer they diffuse throughout the instrument and condense on the insulation. On the addition of moisture, the condensed vapours are converted into acid, which causes a leak across the insulation that is easily mistaken for a gaseous leak due to ionisation. The complete oxidation of phosphorus takes place in two stages, phosphorous oxide being the intermediate product. The first step in the oxidation takes place without the emission of light; the luminescence of oxidising phosphorus is due to the oxidation of phosphorous oxide. Ozone is formed during the oxidation of phosphorous oxide. The failure of certain investigators to detect the formation of ozone in this reaction is due, probably, to the action of phosphorous oxide vapours with the iodine liberated in the usual starch–iodide test. Ozone is formed by the ultra-violet light emitted by glowing phosphorus. J. F. S.

Coagulation of Arsenious Sulphide Sols by Cobaltic Complexes. KICHIMATSU MATSUNO (*J. Coll. Sci. Tokyo*, 1921, **41**, 11, 1—15).—The relationship between the valency of a large number of cobaltammines and their power of coagulating arsenic sulphide sols has been investigated. The effect of ageing of the sol was eliminated by using only such sols as had been kept for a year. The results show that the limiting concentration of the precipitating solution can be expressed by the formula $S_N=S/N^4$, where S_N is

the equivalent concentration of an N valent ion, N the valency of the complex ion, and S the limiting concentration for a univalent ion. This equation may be theoretically deduced from Freundlich's adsorption hypothesis. Using the coagulation method, the author has determined the valency of a number of simple and complex cobaltammine radicles. The chemical changes occurring in aqueous solutions of some of the cobaltammines has been followed by the coagulation method, and the results confirm those obtained in the spectroscopic and conductivity experiments (cf. this vol., ii, 644).

J. F. S.

Metallic Hydrides. I. Alkali Hydrides. FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1921, **4**, 762—781).—The pure hydrides of sodium and potassium have been previously prepared in very small quantities only (Moissan, A., 1902, ii, 136; Elster and Geitel, A., 1910, ii, 379; Keyes, A., 1912, ii, 627). The former is best obtained by leading a rapid stream of hydrogen directly on to the surface of, not into, the metal at such a temperature, above 350°, that a yellow glow is produced, and the hydride is carried away as a white smoke, which is precipitated electrically and filtered through glass wool. At higher temperatures, the vapour is darker owing to volatilisation of metal. Sodium prepared from its azide had no special advantage for this purpose, and negative results were obtained by the use of sodium amalgam or solutions of the metal in liquid ammonia. Potassium hydride was prepared by leading the gas into the metal at 350°. In each case, reaction was facilitated by the presence of metallic calcium. The hydrides of rubidium and cæsium were prepared by heating a mixture of their carbonates with metallic magnesium in hydrogen at 650° for five days and at 580—620° for three days, respectively (cf. Moissan, A., 1903, ii, 367), when 90% and 48% of gas were respectively absorbed. The following are given as the most trustworthy of the results (in mm.) obtained from vapour tension, measurements at intervals of 10° over the ranges of temperatures indicated: Sodium hydride, 300—410°, 15, 17, 21, 27, 38, 55, 87, 136, 201, 285, 396, 540. Potassium hydride, 350—410°, 56, 83, 120, 168, 228, 308, 430; 415°, 509. Rubidium hydride, 370—450°, 100, 114, 130, 160, 200, 253, 322, 424, 567. Cæsium hydride, 340—440°, 78, 100, 126, 160, 202, 256, 317, 402, 503, 630, 787. The results show that there is little or no difference between the values for the different hydrides, and that removal of hydrogen causes some, but no extensive, diminution of the vapour tension, this being less the smaller the atomic weight of the metal, and according with the view that the metal is soluble in the hydride. Previous measurements (Keyes, *loc. cit.*; Troost and Hautefeuille, A., 1874, 767) have really been carried out with such solutions. The results with rubidium and cæsium are quoted with reserve owing to the possibility of the presence of carbon dioxide from the magnesium carbonate formed, although this dissociates very slowly (Marc and Simec, A., 1913, ii, 708); soda-lime was employed to diminish its effect, and the recorded values were quickly attained.

In the case of rubidium, a noteworthy peculiarity, confirmed by repeated observation, consisted in a rapid increase of pressure up to 85 mm. at 230°, followed by a very gradual increase to 100 mm. at 370°, succeeded by rapid increases as above quoted. The reason for this is left indefinite. The results obtained with cæsium hydride are further affected by the considerable sublimation of the metal itself, and also by its solution in the hydride. The latter effect is much more marked in the cases of rubidium and cæsium than in the others. The stability of the pure hydrides increases from cæsium to sodium. J. K.

Alteration of Sodium Carbonate in Air. HUGO DUBOVITZ (*Chem. Zeit.*, 1921, **45**, 890—891).—Commercial sodium carbonate almost always contains a quantity of sodium hydrogen carbonate, the carbon dioxide and water required for the formation of the latter being derived from the atmosphere. After about thirteen days' exposure to air, sodium carbonate may contain from 15 to 20% of the hydrogen carbonate; if the air is very moist and contains a large quantity of carbon dioxide, the conversion of the carbonate into the hydrogen carbonate may be complete. To estimate the amount of sodium hydrogen carbonate in sodium carbonate, a portion of the sample should be heated in a tube connected with a weighed calcium chloride tube; the loss in weight of the two tubes is a measure of the carbon dioxide in the hydrogen carbonate, whilst the gain in weight of the calcium chloride tube is due to the water formed by the decomposition of the hydrogen carbonate and to the moisture in the sample. W. P. S.

Recrystallisation of Metals. The Recrystallisation of Zinc. G. MASING (*Zeitsch. Metallk.*, 1921, **13**, 425—428).—On heating zinc that has been cold-worked, primary recrystallisation of the metal begins immediately throughout the mass without the formation of nuclei. As the temperature rises to 170—190° nuclei of secondary crystals begin to appear in the mass of primary crystals and these gradually increase in number and size if the heating is continued slowly until the whole of the metal consists of a mass of large secondary crystals which are coarser the lower the temperature of formation and the longer the heating. If the metal is subjected to a secondary deformation, the secondary crystal nuclei begin to form at 70°. [Cf. *J. Soc. Chem. Ind.*, 1921, 737A.] A. R. P.

Revision of the Atomic Weight of Zinc. II. Electrolytic Estimation of Zinc in Zinc Chloride. GREGORY PAUL BAXTER and JAMES HALLETT HODGES (*J. Amer. Chem. Soc.*, 1921, **43**, 1242—1251; cf. A., 1916, ii, 327).—The atomic weight of zinc has been redetermined by means of the electrolytic estimation of the amount of zinc in zinc chloride. The method of analysis was the same as that previously used for the analysis of zinc bromide. The zinc chloride used was prepared as follows. Crude zinc was electrolytically transported through a concentrated solution of zinc bromide, and the crystalline sponge of pure zinc thus obtained was thoroughly washed with water and very dilute hydrobromic

acid. It was then immersed in dilute hydrobromic acid and treated with bromine and kept cold. The solution was kept over zinc sponge for three months to remove any traces of cadmium which might be present. The purified solution was fractionally crystallised, using only platinum apparatus. The purest crystals were fused in a platinum boat in a current of nitrogen and hydrogen bromide, dissolved in water, and filtered from traces of carbon and silica. The bromide was crystallised, dried, placed in a quartz boat, and fused in a current of chlorine, and the product used in the analyses. As a mean of eleven analyses, zinc chloride was found to contain 47·970% of zinc, which gives a mean atomic weight 65·372, or, rejecting four relatively low values, 65·379. This value is in good agreement with Richards and Rogers's value 65·376 (A., 1896, ii, 21) and Baxter and Grose's value 65·388 (*loc. cit.*) and indicates that the true atomic weight lies very close to 65·38. J. F. S.

Revision of the Atomic Weight of Cadmium. V. Electrolytic Estimation of Cadmium in Cadmium Sulphate. GREGORY PAUL BAXTER and CARL HENRY WILSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1230—1241; cf. A., 1916, ii, 327).—The atomic weight of cadmium has been redetermined by the electrolysis of anhydrous cadmium sulphate. Preliminary experiments with the hydrated salt showed that this salt generally contains a small amount of water above that required for the composition $CdSO_4,8/3H_2O$, and since such water cannot be removed, the hydrated salt is unsuitable for atomic weight determination. Anhydrous cadmium sulphate was prepared from the hydrated salt by heating at 200° in a current of air for two hours when most of the water was removed, the heating was then continued at 720° in a current of sulphur trioxide until a constant weight was obtained. After cooling, the product was heated at 200° for a further two hours to remove sulphur trioxide. The weighed sulphate was dissolved in water and electrolysed, using a weighed mercury cathode in the same way as previously described (*loc. cit.*). As the result of eleven analyses, the value 112·409 was obtained for the atomic weight, the extreme values being 112·328 and 112·437. The mean of the whole of the work of the author and his collaborators on the atomic weight of cadmium is 112·411. The preliminary experiments on the hydrated salt gave a value 112·04. J. F. S.

Physical Chemistry of the Oxides of Lead. I. The Solubility of Lead Monoxide. SAMUEL GLASSTONE (T., 1921, **119**, 1689—1697).

Theory of Smelting. IV. Equilibrium between Metal-pairs and Sulphur. The System: Copper–Manganese–Sulphur. W. GUERTLER and K. L. MEISSNER (*Metall. u. Erz*, 1921, **18**, 438—443; cf. this vol., ii, 402, 589). On melting manganese with copper sulphide, the mass separates into two layers, the upper consisting of manganese sulphide or of a eutectic of manganese and cuprous sulphides and the lower of pure copper or of mixed

crystals of copper and manganese, according to the proportions of both metals present. Manganese has, therefore, a greater affinity for sulphur than copper, and this affinity is not modified by the addition of iron. Thus, if to a mixture of molecular proportions of cuprous sulphide with 1 atomic proportion of manganese, iron is added, the mass separates into three layers, an upper layer of manganese sulphide, a middle layer of a eutectic mixture of manganese sulphide and iron, and a lower layer of copper more or less mixed with iron. A. R. P.

The Constitution of the Alloys of Copper with Tin. III. and IV. J. L. HAUGHTON (*J. Inst. Metals*, 1921, **25**, 309—330; cf. A., 1915, ii, 689).—A study of the equilibrium diagram of copper–tin alloys containing 30—100% of tin at temperatures below 250° by thermal curves and electrical resistance measurements. The alloy with 30·5% of tin shows no arrest between 150° and 250°. The alloy with 42·8% of tin shows a small arrest at about 190°. The alloy containing 57% of tin shows a greater arrest at 190° and in addition a slight arrest at about 210°. These two arrests are present in alloys containing 59% and 61% of tin. At 63% of tin the 190° arrest is pronounced and the 210° point has vanished and a new one has taken its place at 226°. As the percentage of tin increases the size of the higher arrest increases and the size of the lower arrest decreases, being barely perceptible at 90% of tin. The 210° arrest is not affected by the rate of heating whereas on rapid heating the 190° arrest will not show. After the 190° arrest has been suppressed, slow heating or cooling curves do not again show it until the sample has been annealed. Repeated heating and cooling at a slow rate bring about the disappearance of the 190° arrest from heating curves although it persists on the cooling curve. Electrical resistance measurements confirmed the presence of the 190° and 210° arrests. The arrest at 190° is caused by an allotropic change in the ϵ-constituent. The arrest at 226° is due to the solidification of the eutectic of the constituents ϵ and ζ. The latter is a dilute solid solution of copper in tin. The author cannot explain the cause for the appearance of the 210° arrest. A study of the equilibrium curve between 99 and 100% of tin showed that the solubility of copper falls off slightly with increasing tin content but that the slope of the curve is too small to show in the equilibrium diagram. In an appendix the author discusses the diagrams for copper–tin alloys suggested by other workers. CHEMICAL ABSTRACTS.

Stages in the Recrystallisation of Aluminium Sheet on Heating, and Birth of Crystals in Strained Metals and Alloys. H. C. H. CARPENTER and CONSTANCE F. ELAM (*J. Inst. Metals*, 1921, **25**, 259—280).—By heating for long periods at 220°, and for short periods at 250° and 300°, there is produced a general tarnishing of the surface, a granular structure, and a blurring of the original boundaries of the flattened crystals. The birth of new crystals in the old boundaries takes place in the early stages of recrystallisation at 250° and 300°. The structure obtained

after heating to structural equilibrium at a given temperature appears in two distinct forms. New evidence is offered in support of views already put forward (*ibid.*, 1920, **24**, 83) on the birth of crystals. CHEMICAL ABSTRACTS.

The Function of Water of Crystallisation in the Behaviour of Permutite. A. GÜNTHER-SCHULZE (*Zeitsch. Elektrochem.*, 1921, **27**, 402—406).—Experiments were made to determine whether any relation exists between the water content of the permutite molecule and the mobility of the kation which is expressed in the readiness with which basic exchange takes place. The permutites of the alkali and alkaline-earth metals contain $5H_2O$, and it is generally considered that, of these, three are water of crystallisation and two "water of constitution." Experiments with potassium permutite, however, showed that the water content varies continuously according to the temperature and vapour pressure, and no distinction was found between the first three and the last two molecular proportions. The molecular volume of potassium permutite was determined at different stages of hydration, and it was found that the increase of volume per molecule of water was in proportion to the number of molecules of water added. So long as the permutite is not completely dehydrated, it can again be fully hydrated, but after ignition it takes up only about $1{\cdot}25H_2O$. The permutites of the metals copper, silver, chromium, and aluminium, formed by basic exchange from alkali metal permutites, contain from 6 to $8H_2O$; but when formed from ignited potassium permutite the water deficiency of this persists in the derived permutites. The mobility of the kation does not appear to be influenced by the water content. Ignited potassium permutite comes to the same point of equilibrium with a silver nitrate–potassium nitrate solution, for instance, as the fully hydrated permutite, but equilibrium is reached much more slowly, because, through partial sintering during ignition, the high porosity of the manufactured permutite is lost. The ignited permutite is very similar in character, in fact, to natural zeolites. E. H. R.

Preparation of Colloidal Manganese Dioxide. EUSTACE J. CUY (*J. Physical Chem.*, 1921, **25**, 415—417).—The older methods for preparing colloidal manganese dioxide are enumerated and a new method is described. The method described consists in heating a $N/20$ solution of potassium permanganate to the boiling point and while stirring, adding concentrated ammonia solution at the rate of one drop every three to four minutes, until the solution has passed through a wine-red tint and become deep coffee coloured. At no period of the addition may the solution have a perceptible odour of ammonia. To test the complete absence of permanganate in the brown solution, a little is treated with sodium chloride solution which coagulates the colloidal manganese dioxide and leaves the characteristic colour of permanganate. The product contains only potassium hydroxide as an impurity, and as this substance has no action on the colloid, it may be left in the solution. The colloid is immediately coagulated by contact with paper and

parchment, and is therefore purified with great difficulty. It catalyses the decomposition of hydrogen peroxide and is perfectly stable in the presence of alcohol of all concentrations. J. F. S.

The Electrolytic Production of Sodium and Potassium Permanganates from Ferromanganese. ROBERT E. WILSON, W. GRENVILLE HORSCH, and MERRIL A. YOUTZ (*J. Ind. Eng. Chem.*, 1921, **13**, 763—769).—The electrolytic cells used in these experiments consisted of a cylindrical glass jar containing a porous porcelain cup which served as a diaphragm, the cathode (of 16-gauge sheet iron) being placed in the cup and the ferromanganese anode in the jar outside. Several cells were operated in series across a source of direct current. The circuit also contained an ammeter, a copper coulometer, and a rheostat. Arrangements were made for connecting a voltameter across any individual cell. The temperature of each cell was determined by means of a thermometer placed near to the anode. The average period of a run was five hours. The tabulated results of a large number of experiments are given, from which it is concluded that the most suitable anolyte is a solution of sodium carbonate, which gives a product uncontaminated by manganese, with the best efficiency and with the least expenditure of power. The percentage of manganese in the anode has little effect on the cell voltage, but increased manganese content gives increased current efficiency. With a 40% manganese anode (Spiegeleisen), practically no permanganate is produced. The commercial ferromanganese containing 80% of manganese was found to be the most suitable material. The presence of copper in the anode produced practically no effect, but 2% of cobalt reduced the efficiency almost to zero. The operating temperature should not be higher than about 10—20°, as increase of temperature lowers efficiency, increases the energy consumption, and gives rise to a " skin effect " which causes excessive voltages. A current density of about 6 amperes per sq. dcm. gives the minimum energy consumption. At lower current densities the current efficiency falls rapidly; at higher current densities it rises slowly but is accompanied by increased energy consumption. The effect of all variables such as current density, temperature, anolyte composition, etc., is stated to be due to the variations caused by these factors in the oxygen overvoltage, a high oxygen overvoltage being necessary for high current efficiencies in permanganate production. S. S. A.

Magnetic Determinations of A_0, A_1, A_2, and A_3 Points in Steels containing up to 4·8 per cent. of Carbon. TORAJIRÔ ISHIWARA (*Sci. Rep. Tōhoku Imp. Univ.*, 1920, **9**, 401—415; cf. A., 1913, ii, 222).—The specimens examined numbered twenty-two, and ranged from pure iron to steel containing 4·81% of carbon; the determinations were made by a magnetometric method and with a torsion balance, and the heating was effected in a vacuum. The results obtained are discussed fully, and are recorded in tabular form and also in a series of graphs. W. P. S.

Chemical Equilibrium between Iron, Carbon, and Oxygen. A. MATSUBARA (*Trans. Amer. Inst. Mining Met. Eng.*, 1921, No. 1051, 52 pp.).—An investigation of (1) the equilibrium composition of the gas phase in the system: carbon monoxide–carbon dioxide–iron (containing 2 to 30% of oxygen) at 873°, 1070°, and 1175°; (2) the equilibrium composition of the gas phase in the systems (*a*) carbon monoxide–carbon dioxide–ferrous oxide (saturated with iron)–iron (saturated with ferrous oxide) and (*b*) carbon monoxide–carbon dioxide–ferrosoferric oxide (saturated with ferrous oxide)–ferrous oxide (saturated with ferrosoferric oxide) at several temperatures above 700°; (3) the equilibrium composition of the gas phase in the systems (*a*) ferrous oxide–iron carbide (Fe_3C)–carbon monoxide–carbon dioxide, and (*b*) iron–iron carbide–carbon monoxide–carbon dioxide in the range 700° to 1100°. The specific reactions considered are: (i) $3Fe_2O_3+CO \rightleftharpoons 2Fe_3O_4+CO_2$; (ii) $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$; (iii) $FeO+CO \rightleftharpoons Fe+CO_2$; (iv) $2CO \rightleftharpoons C+CO_2$; (v) $3Fe+2CO \rightleftharpoons Fe_3C+CO_2$; (vi) $3FeO+5CO \rightleftharpoons Fe_3C+4CO_2$. The first period of carburising reaction apparently coincides with the latter, and a later period with the former of the last two reactions. There exist also transient equilibria between reactions (v) and (vi), (v) and (iii), (vi) and (iv). Equilibria at lower temperatures occur with a more oxidised form of the solid phase than at higher temperatures, even in the same carburising reaction. The limits of temperature and pressure for carburisation are determined from the experimental data. Above 1300° the carburising action of carbon monoxide does not occur; carburised iron is oxidised to a ferrous oxide–iron solid solution by pure carbon monoxide at 1 atmosphere pressure. Under 1 atmosphere pressure, at 1200°, neither carburisation nor decarburisation occurs in pure carbon monoxide; between 1200° and 1300°, iron containing carbon is decarburised by pure carbon monoxide, but iron containing oxygen may be carburised by the same gas, both reactions ending in the formation of oxygenated carboniferous iron proper to that temperature. Between 695° and 1200° a gas sufficiently rich in carbon monoxide will carburise iron; below 695°, no true carburisation can occur. CHEMICAL ABSTRACTS.

Stereochemical Configuration of the Aquo-triammine and Diammine Cobalt Complex Salts. KICHIMATSU MATSUNO (*J. Coll. Sci. Tokyo*, 1921, **41**, 10, 1—27).—The absorption spectra of aqueous solutions of the eight aquo-cobaltammines,

$$\left[Co\genfrac{}{}{0pt}{}{H_2O[1]}{H_2O[2]}en_2\right]Cl_3,2H_2O;\quad \left[Co\genfrac{}{}{0pt}{}{H_2O[1]}{H_2O[6]}en_2\right]Cl_3,2H_2O;$$

$$[CoCl(H_2O)_2(NH_3)_3]SO_4;\ [CoCl_2H_2O(NH_3)_3]Cl;$$

$$[CoCl_2(H_2O)_2(NH_3)_2]SO_4H;\ [CoCl(H_2O)_3(NH_3)_2]SO_4,H_2O;$$

$[Co(H_2O)_3(NH_3)_3]Cl_3$ and $[Co(H_2O)_3(NH_3)_3]Cl_3$ have been measured over a wide range of concentrations. The electrical conductivity of six complex cobaltammines has also been measured at intervals over periods of time. From the results, the author has demonstrated the influence of the co-ordinated water molecules and has drawn the configurations of the compounds. Two new complex

compounds have been obtained, trans$[Co(NH_3)_3(H_2O)_3]Cl_3$ and $[Co(NH_3)_3C_2O_4{\cdot}NO_3]$. The complex compound prepared by Werner by the action of silver nitrate on $[CoClC_2O_4(NH_3)_3]$ and given the formula $[Co(NH_3)_3C_2O_4(H_2O)_2]NO_3$ is shown to have the formula $[Co(NH_3)_3C_2O_4NO_3]H_2O$. An explanation is given of the substitution reactions of the cobaltammines which have the radicles of strong acids in the nucleus. J. F. S.

Reduction of Chromium and other Difficultly Reducible Metals. H. C. P. WEBER (U.S. Pat. 1373038).—A mixture of chromic chloride with iron is heated to 700—1200° to produce metallic chromium and volatilise ferric chloride. If the iron is sufficiently finely divided, and a relatively low temperature is employed for reduction, chromium is obtained in finely divided form. If solid pieces of iron are used and the reaction takes place below the m. p. of the metals, a coating of chromium is formed on the pieces of iron. If an excess of iron is used and a sufficiently high temperature is employed, an alloy of chromium and iron is produced. Chlorides of chromium and nickel may be similarly reduced together to form alloys or mixtures with each other or with iron. Chromic oxide may be employed and converted into chloride with carbon and chlorine. The reduction process is advantageously carried out in a vacuum or in an inert atmosphere such as nitrogen. Other refractory metallic compounds may be similarly reduced and alloyed. CHEMICAL ABSTRACTS.

The Existence of Gaseous Hydrides of Zirconium and Thorium. ROBERT SCHWARZ and ERICH KONRAD (*Ber.*, 1921, **54**, [*B*], 2122—2133).—The question of the existence of gaseous hydrides of zirconium and thorium is of considerable theoretical interest since, if producible, they would form exceptions to Paneth's rule (A., 1920, ii, 749). The preparation of volatile zirconium hydride has been claimed by Winkler (A., 1890, 1375), but denied by Wedekind (A., 1913, ii, 225), whilst preliminary experiments by Schwarz and Deissler (A., 1920, ii, 42) have pointed to its existence. The formation of thorium hydride is recorded by Klauber and von Mellenheim (this vol., ii, 206). Evidence of the existence of either hydride in the gaseous state has not now been obtained.

The experiments are performed by heating the pure respective dioxides with magnesium, dissolving the products in hydrochloric acid and leading the volatile and dried gases, mixed with purified hydrogen, through a series of strongly ignited Marsh tubes. In general, small mirrors are thus obtained which are shown to consist mainly of silicon; the presence of zirconium or thorium could not be detected in any instance. In addition to silicon hydride, the gases evolved contain small amounts of the hydrides of phosphorus and sulphur.

Reduction of the zirconium dioxide by magnesium is effected in iron crucibles which have been coated internally with an electrolytic deposit of nickel and are provided with a gas-tight iron lid so arranged that a current of hydrogen may be passed through the apparatus. Unsatisfactory results were obtained by heating the

mixture in an electric furnace at about 1000°, or by its ignition by a thermite mixture or magnesium ribbon; satisfactory products are most readily secured by gradually heating the crucible almost to bright redness in a blowpipe flame.

All possible precautions are taken to eliminate the possibility that the non-observance of a metallic mirror is due to the rapid decomposition of the gaseous hydrides before reaching the Marsh tubes. H. W.

Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride and Bismuth Bromide. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1921, **54**, [*B*], 1873—1904).—A detailed account of work of a portion of which a preliminary notice has appeared previously (A., 1920, ii, 549).

Two series of analyses of bismuth chloride and bismuth bromide are recorded. In each series, the atomic weight is determined by two independent methods (gravimetric estimation of the ratios $BiCl_3 : 3AgCl$ and $BiBr_3 : 3AgBr$ and nephelometric measurement of the silver haloid dissolved in the mother-liquor and determination of the ratios $BiCl_3 : 3Ag$ and $BiBr_3 : 3Ag$ by gravimetric titration with the aid of the nephelometer). In all, eight independent mean values of the atomic weight are thus obtained, the extreme results being 208·98 and 209·00 on the basis Ag=107·88. The values recorded previously (*loc. cit.*) are rendered slightly uncertain by the subsequent observation that the silver condensing tube used in the preparation of the water was giving small amounts of silver ions to the latter (the effect is due to access of laboratory air) and it is only possible to apply an estimated correction. The mean value of the six most trustworthy series is Bi=208·997 or, in round numbers, 209·00; this is a unit higher than the international value previously adopted. The titrimetric values are regarded as the most trustworthy of all and twenty-two estimations are recorded in which the maximal difference in the individual results is 0·5 : 10000.

The experiments differ from the usual type of such determinations in that, in order to prevent the precipitation of basic bismuth salts, it is necessary to precipitate the chloride and bromide in 3*N*- and 2*N*-nitric acid solution respectively. This is shown to be without effect on the results by a special series of experiments with potassium chloride and bromide.

The recent determinations of the atomic weight of bismuth by Classen and Ney (this vol., ii, 119), which depend on the conversion of bismuth triphenyl to bismuth oxide, are criticised in detail. Recalculation of their figures on the basis C=12·001 and H=1·0077 gives the value Bi=208·91±0·05 which is 0·09 lower than that calculated by the authors. H. W.

Thermal Analysis of Binary and Ternary Alloys. J. WÜRSCHMIDT (*Zeitsch. Physik*, 1921, **5**, 39—43).—Cooling and heating curves have been produced for bismuth and tin and for a series of alloys of these metals. Similar experiments have been made with a series of ternary alloys of lead, bismuth, and tin and curves produced. The temperature measurements were made

with an iron–constantan thermo-element which made it possible to work with much smaller quantities of material than is usual. In the case of the binary alloys, the complete fusion diagram has been produced, and from this it is shown that the eutectic contains 46 atom % of bismuth and melts at about 140°. In the ternary alloys, the eutectic corresponds with the composition Bi_2SnPb and has a melting point of 96°. J. F. S.

The Chemical Properties of Alloys. G. TAMMANN (*Zeitsch. Metallk.*, 1921, **13**, 406—419).—The physical properties of binary alloys of two metals that form a continuous series of mixed crystals change regularly with varying composition, whereas their chemical properties alter suddenly when the atomic ratio of the metals present exceeds a certain well-defined limit, which may generally be expressed as $n/8$, where n, usually 1, 2, 4, 6, 7, rarely 3 or 5, is the number of atoms of the more noble metal in every 8 metal atoms. Thus, yellow ammonium sulphide blackens, in the cold, all alloys of gold and copper containing less than 50·8% of gold (atomic ratio 2/8 Au), whilst those richer in gold remain untarnished even after four years' immersion. Again, nitric acid dissolves silver completely from gold–silver alloys containing less than 52·5% of gold (atomic ratio 3/8 Au), partly from those containing 52·5—64·6 of gold (atomic ratio 4/8 Au), and not at all from those still richer in gold. Under certain conditions, however, these limits disappear, that is, the atoms of the active component tend to diffuse towards the surface, so that the surface layer falls below the limiting value. In the case of the copper–gold alloys, hydrogen sulphide, which behaves like ammonium sulphide at ordinary temperatures, attacks alloys richer in gold as the temperature rises, until, at 140° it blackens gold containing only 1% of copper. A theoretical explanation of the above phenomena, based on the space-lattice theory of crystal structure, is given in some detail and it is shown that it is possible to prepare what may be called "space-lattice isomerides" of alloys which behave differently towards certain reagents. The electrochemical behaviour of binary alloys may be studied by measuring the *E.M.F.* of cells in which the electrolyte consists of a salt of the more electronegative metal from which one pole is made, whilst the other pole consists of different alloys of the two metals. If the composition of the latter is plotted against the voltage of the cell, the curve obtained for alloys in which inner diffusion takes place (for example amalgams) resembles a hyperbola concave to the axis of composition, whilst that obtained for alloys of metals (for example copper–manganese) which form a continuous series of mixed crystals, in general, runs close to this axis until a certain definite composition is reached, when it rises in a nearly perpendicular straight line to a constant voltage equal to that of a cell in which the poles consist of the two pure metals. Alloys of gold with copper and silver behave somewhat differently, the curve rising, after a certain percentage of gold, in a straight line to the value for pure gold, probably due to the deposition of a fine film of the latter on the surface of the alloy. Two metals that form several series of mixed

crystals, for example zinc and copper, give alloys that yield similar curves as manganese–copper except that there are a number of steps corresponding with the various series of mixed crystals, but these steps do not correspond with any definite atomic ratio between the elements. Gold–copper alloys, when made the anode in an electrolytic cell containing a solution of copper nitrate are attacked without evolution of oxygen if the gold does not exceed 29 atoms %, copper dissolving from the alloy. If the voltage applied to a cell containing a large copper cathode and a small anode of gold–copper alloy is plotted against the amperage the curves for alloys containing 25—28 atoms % of gold show a peculiar double hump, whereas the curves for alloys richer or poorer in gold are roughly parabolic. The decomposition voltage of the series is at a maximum at nearly the same limit as that at which there is no attack by reagents, namely, 27 atoms % of gold, while polarisation is first noticeable with alloys containing 50 atoms % of gold. Alloys containing more gold behave in these two cases like pure gold. A. R. P.

Preparation of Pure Platinum. EDWARD WICHERS (*J. Amer. Chem. Soc.*, 1921, **43**, 1268—1273).—Commerical platinum containing small quantities of rhodium, palladium, and iridium, as well as considerable quantities of iron, tin, and other base metals, may be freed from these impurities by four precipitations of ammonium platinichloride. The method consists in dissolving the metal in aqua regia, removing excess of nitric acid by repeated boiling with hydrochloric acid, and precipitating with ammonium chloride. The precipitate is drained on a Buchner funnel, stirred with a considerable volume of 15—20% ammonium chloride solution, and again drained; the washing is repeated three or four times. The washed precipitate is dried and ignited to sponge in an electrically heated muffle. The sponge is dissolved in aqua regia and the process repeated four times. The amount of platinum left in the mother-liquor does not exceed 1% of the platinum in the precipitate. The final precipitate is ignited to sponge in a porcelain dish over a gas flame, and during the reduction a current of hydrogen is passed over the material. The metal was tested for purity by spectroscopic examination and by measuring its thermo-electric effect against a very pure piece of Heraeus wire. The samples were melted to buttons in an oxy-hydrogen flame on a lime slab and then rolled into ribbons. Spectroscopically, the ribbons were found to be pure except for calcium and very often magnesium, but those which had been prepared by melting in an oxy-hydrogen flame containing an excess of oxygen contained less calcium than those prepared in the ordinary oxy-hydrogen flame. Strips prepared in the ordinary oxy-hydrogen flame gave considerable positive *E.M.F.* values against the standard wire at 1200°, whilst those prepared in the flame with excess of oxygen gave negative values varying from 2 to 38 micro-volts in the same circumstances. The calcium taken up by the platinum is in the form of metal, produced from the lime by the reducing atmosphere. The amount of calcium taken up by the platinum in the above-named circumstances can be considerable,

and in some cases the platinum is alkaline to moist litmus. The purest platinum yet obtained contains 0·0001% of calcium. Melting platinum in magnesia crucibles yields a brittle button which cannot be rolled, and in some cases the button was found to contain 3% of magnesium. J. F. S.

Mineralogical Chemistry.

Nature and Chemical Composition of a Mineral containing Cobalt found at Katanga. A. SCHOEP (*Bull. Soc. chim. Belg.*, 1921, **30**, 207—212).—A colloidal mineral allied to heterogenite (cf. Frenzel, this Journal, 1872, 990) and schulzenite (cf. Maertens, A., 1896, ii, 529) and resembling lustrous anthracite in appearance, has been found embedded in malachite and chrysocolla. Its composition is estimated to be $3Co_2O_3,CoO,CuO,7H_2O$. J. H. L.

The Chemical Constitution of Silicates. B. GOSSNER (*Centr. Min.*, 1921, 513—525).—A theoretical paper in which the author criticises current views as to the chemical constitution of silicates. Attempts to deduce from the chemical composition of a crystal the constitution of the corresponding molecular unit are fallacious. It is pointed out that the existence of complex silicates such as $(SiO_4)_3Al_2Ca_3$ or Si_3O_8AlK at the high temperatures at which the corresponding minerals were formed is most improbable, for the chemical affinities of silica and alumina, slight at ordinary temperatures, diminish at higher temperatures. For similar reasons, the existence in minerals of such radicles as $—Al(OH)_2$ is inconceivable. The author endeavours to show that, by postulating the existence of a limited number of simple stable silicates as molecular individuals, the structure of more complicated silicates can be explained as due to combinations of these. Without inquiring further into the nature of the combination of the simpler silicates to the more complex forms, this may be taken as similar to that existing in crystalline double salt or in solid compounds containing water of crystallisation. The simple silicates postulated are SiO_3Na_2, SiO_3Ca, SiO_3Mg, SiO_2,Al_2O_3, all of which can readily be obtained crystalline from the fused state. When water is a constituent of a silicate crystal, hydroxides such as $Ca(OH)_2$ or $Mg(OH)_2$ may be present, and, in certain circumstances, AlO_2H and AlO_3H_3, both of which are known in the crystalline state. From this point of view the composition of several groups of minerals is discussed, particularly in relation to the paragenesis of the minerals. As an example, in the alkali–lime–silicate group, the following formulæ are given:

Nepheline, $SiO_3Na_2,[SiO_2,Al_2O_3]$.
Leucite, $SiO_3K_2,[SiO_2,Al_2O_3],2SiO_2$.
Albite, $SiO_3Na_2,[SiO_2,Al_2O_3],4SiO_2$.
Anorthite, $SiO_3Ca,[SiO_2,Al_2O_3]$.

These formulæ bring out well the relationships between the minerals of this group, the fact that nepheline and anorthite have sharp melting points whilst the others have not, and that the former pair more readily undergo secondary changes in geological deposits, for instance into zeolites, whilst the others behave as if they were in a sense more saturated. A number of other groups are also discussed. E. H. R.

Analytical Chemistry.

Application of the Immersion Refractometer to the Analysis of Aqueous Salt Solutions. C. A. CLEMENS (*J. Ind. Eng. Chem.*, 1921, **13**, 813—816).—Where n=the refractive index of solution, n_0=the refractive index of water of the same temperature, and c=grams of solute per 100 c.c. of solution, $n-n_0/c$ is a constant. Thus $c/n-n_0$ is a constant independent of temperature, unaffected by dissociation, hydration, and the formation of complexes, and represents the percentage by volume of salt equivalent to one division of the immersion refractometer scale. In determining the composition of mixtures of two salts, one of known and the other of unknown concentration, the percentage of the salt of known concentration divided by its refractive index factor gives in terms of scale divisions the effect on the refractive index due to that salt, and when this value is subtracted from the refractive index of the solution containing the two salts the remainder is equivalent to the refractive index of the salt of unknown concentration in aqueous solution. In the case of two salts both of unknown concentration the specific gravities of the solutions d_4^{20} were taken and the value for water was subtracted. The values thus obtained were then divided by the respective percentages by volume of salt in the solutions. This gave the effect of the addition of 1% of salt on the density of the solution at 20°. The density of a solution at 20° can be calculated by means of the factors thus obtained by multiplying the factor by the percentage of the salt and adding the value for water. By reversing the process, the percentage of salt can be found from the density. Knowing the refractive index of the solution and of water at the same temperature and d_4^{20} of the solution, the percentage by volume of the two salts can be calculated. S. S. A.

Measurement of Hydrogen-Ion Concentration. G. W. MONIER-WILLIAMS (*Analyst*, 1921, **46**, 315—324).—The construction of an inexpensive apparatus, and the method of using it for the determination of hydrogen-ion concentrations, are fully described. W. P. S.

Joint Use of Two Indicators in the Titration of Acids and Bases. J. L. LIZIUS (*Analyst*, 1921, **46**, 355—356).—The joint

use of two indicators, phenolphthalein and thymolphthalein, or methyl-red and thymol-blue, is recommended, since the colour changes denote either the approach of the end-point or the fact that the solution has been over-titrated. W. P. S.

Rapid Electroanalysis. ARNOLD LASSIEUR (*Bull. Soc. chim.*, 1921, [iv], **29**, 754—780).—A lecture delivered before the French Chemical Society. W. G.

System of Qualitative Chemical Analysis for the Positive Ions. CLAUD H. HALL, jun. (*Trans. Maryland Acad. Sci.*, 1921, **4**, 8 pp.).—The first group is precipitated by means of red phosphorus instead of by hydrochloric acid; this serves to bring mercury entirely into this group and places all the lead in the second group. Thioacetic acid, or its ammonium salt, is substituted for hydrogen sulphide. In the alkali group, potassium is precipitated by means of phosphotungstic acid. CHEMICAL ABSTRACTS.

Estimation of Water in Alcohols. TH. WIRTH (*Zeitsch. Deut. Oel-Fett. Ind.*, 1921, **41**, 147).—Five grams of calcium hydride granules are covered with xylene (previously dried by boiling with calcium hydride) and the mixture is boiled for a moment to dislodge air adhering to the solid; the air in the flask is displaced by pure dry carbon dioxide. The gas is admitted for the duration of the estimation at the rate of two bubbles per second, the exit tube leading to a gas burette containing potassium hydroxide solution. About 1 gram of the alcohol is drawn into the flask from a dropping funnel which is rinsed with 10 c.c. of xylene. Evolution of hydrogen, half of which is derived from the water according to the equation: $CaH_2+H_2O+CO_2=CaCO_3+2H_2$, begins immediately and is complete in forty-five minutes. CHEMICAL ABSTRACTS.

Estimation of Hydrogen Peroxide by means of Stannous Chloride. SVEN HASSELSKOG (*Svensk. Farm. Tid.*, 1921, **25**, 149—150).—The method for the estimation of hydrogen peroxide proposed by Bertalan (A., 1916, ii, 393) is not trustworthy. There is not a single simple reaction involved as claimed. Two other by-reactions occur, namely: $SnCl_2+xH_2O_2 \rightleftharpoons SnO_2,xH_2O+Cl_2+(x-2)O$ (see Zsigmondy, "Kolloidchemie," 2nd. ed.) and $2HCl+H_2O_2 \longrightarrow 2H_2O+Cl_2$. CHEMICAL ABSTRACTS.

Electrometric Estimation of Bromate, Dichromate, Nitrite, and Chloride Ions. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1309—1317; cf. this vol., ii, 411).—A continuation of previously published work (*loc. cit.*). In the present paper the author describes methods for the electrometric titration of the ions named in the title. The estimation of bromate by means of iodide and permanganate is effected as follows: A known excess of iodide solution is placed in the titration vessel, which is fitted with a mechanical stirrer and electrodes as previously described (*loc. cit.*) and sufficient $10N$-sulphuric acid added to make the solution double normal. The bromate solution is then

added in such quantity that about 10% of the iodide is undecomposed. The stirrer is started rotating and when the voltage becomes steady the excess of iodide is determined by titration with potassium permanganate solution. The method is accurate to about 0·08%, and the presence of chlorate ions does not influence the results. Iodide solutions may be directly titrated with bromate solution in the presence of $2N$-sulphuric acid, the end-point being given by an abrupt rise in the potential. This estimation may be carried out in the presence of hydrochloric acid, but difficulties are experienced which become greater the greater the concentration of the acid and so render the accuracy in the presence of hydrochloric acid doubtful. Iodide may be titrated directly with dichromate in sulphuric acid solution of at least $2N$ strength, if sufficient time is allowed near the end point for the reaction to come to an end. The results in this case are accurate to 1 in 6300. Nitrous acid and nitrites may be estimated by the electrometric method as follows: a known quantity of permanganate solution is placed in the titration vessel, diluted, and $10N$-sulphuric acid added to make the final concentration $1·5N$. The stirrer is started and the nitrite solution slowly added so as to leave 5—10% of the permanganate unchanged. After about five minutes a known excess of iodide is added and the titration completed with permanganate solution. The method gives results which are equally as good as those obtained by the method of Laird and Simpson (A., 1919, ii, 242). The chloride ion may be estimated by adding an excess of a silver solution to a solution of chloride and stirring to coagulate the precipitate. The solution is filtered into the titration vessel, acidified with sulphuric acid, and treated with a measured excess of iodide solution, the excess of which is determined by titration with permanganate. The results are accurate to 1 part in 750 parts, but the method is involved and long. J. F. S.

Estimation of Sodium Hyposulphite. James Hollingsworth Smith (*J. Amer. Chem. Soc.*, 1921, **43**, 1307—1308).—The methods available for the estimation of sodium hyposulphite have been critically investigated with the object of finding a fairly rapid method in which it is unnecessary to ensure complete absence of air. The methods due to Ekker (A., 1894, ii, 479), Fradiss (A., 1900, ii, 44), and to Knecht and Hibbert (A., 1907, ii, 907) are all considered to be unsatisfactory for various reasons; the two first-named methods because of the action of air on the solutions and the last method because of the difficulty of preparing pure solutions of dyes of known composition and of the difficulty of working with solutions of titanous chloride. The method of Seyewetz and Bloch (A., 1906, ii, 578), which consists in oxidising the hyposulphite with an ammoniacal solution of silver chloride, according to the equation

$$Na_2S_2O_4+2AgCl+4NH_4{\cdot}OH=2(NH_4)_2SO_3+2NaCl+2H_2O+2Ag,$$

and weighing the silver, suffers from two defects, first the gravimetric procedure is slow, and, secondly, it is inaccurate because of the insoluble impurities in the hyposulphite which are held back by the filter and weighed with the silver. The author has modified

the process so that both defects are removed. The precipitated silver is filtered on a Gooch crucible, washed, and then dissolved in nitric acid and estimated by the Volhard method. A further modification consists in using silver nitrate instead of silver chloride. The modified method is carried out as follows: about 0·4 gram of hyposulphite is placed in a dry beaker and treated with double the theoretical quantity of ammoniacal silver nitrate solution. The hyposulphite dissolves and is immediately oxidised with the precipitation of metallic silver. The solution is filtered without warming on a Gooch crucible and washed free from silver salts with an ammoniacal solution of ammonium nitrate. The crucible is then placed in nitric acid and warmed to dissolve the silver and remove nitrous acid. The crucible is removed and the solution diluted and titrated with 0·1*N*-potassium thiocyanate solution. The method is rapid and accurate. J. F. S.

Estimation of Hyposulphites and Sulphoxylates. EDWARD L. HELWIG (*Amer. Dyestuff Reporter*, 1920, **7**, ii, 12—13).—Sodium hyposulphite is added in small quantities from a weighing bottle to 50 c.c. of a standard ammoniacal cupric sulphate solution (50 grams of crystallised copper sulphate and 10 c.c. of concentrated ammonia solution per litre) in a flask through which carbon dioxide is being passed, until the blue colour is discharged. The reaction is: $2CuSO_4+4NH_3+Na_2S_2O_4+2H_2O=Cu_2SO_4+Na_2SO_3+(NH_4)_2SO_3+(NH_4)_2SO_4$. An excess of hyposulphite causes the precipitation of 1/13·68 part of metallic copper. For the analysis of sodium sulphoxylate-formaldehyde ("formopon"), standard copper solution is added from a burette to an aqueous solution of the salt through which carbon dioxide is being passed; the liquid is then boiled and the copper solution added until a faint permanent blue colour is obtained. Basic zinc sulphoxylate-formaldehyde ("formopon extra") is dissolved in ammonia solution and estimated in a similar manner. CHEMICAL ABSTRACTS.

New Procedure for the Estimation of Arsenic. J. CRIBIER (*J. Pharm. Chim.*, 1921, [vii], **24**, 241—246).—A new method for the estimation of small quantities of arsenic is based on the intensifying and fixing action of potassium iodide on the yellow stain produced by hydrogen arsenide on mercuric chloride paper. The similar stains produced by the hydrides of antimony, sulphur, and phosphorus are not altered by potassium iodide in this way. The apparatus consists of a flask fitted with a vertical glass tube about 5 mm. in diameter and 30 cm. long. The lower end in the flask is drawn out to a dropping tube and a hole in the tube about 2·5 cm. from the bottom allows of the egress of the gas. For each estimation 8 grams of zinc and 60 c.c. of 20% sulphuric acid are used, and the arsenical solution, previously oxidised with a few drops of permanganate to convert sulphur and phosphorus compounds into non-reducible sulphuric and phosphoric acids, is added all at once. The lower part of the vertical tube contains a roll of filter-paper about 10 cm. long to absorb moisture carried up mechanically by the gas. The upper part of the tube contains the band of mercuric

chloride paper, 5 mm. wide and 12—15 cm. long, extending to within 2 cm. of the roll of filter paper. When all the arsenic is eliminated, which requires two to six hours or more, the test paper is treated with 10% potassium iodide solution, which, acting specifically on the arsenic stain, turns it brown, and at the same time renders it permanent to light and moisture. The arsenic is estimated by comparison of the stain with those produced by known quantities under similar conditions. From 0·0001 to 0·1 mg. can be estimated by the above procedure. G. F. M.

Estimation of Carbon in Aluminium. J. A. SONDAL (*Tidskr. Kem.*, 1920, **17**, 234—245).—Carbon present in commercial aluminium in amounts varying between 0·012 and 0·087% is estimated by treating the metal with potassium cuprichloride solution and weighing the residue, or by an adaptation of the wet combustion method of Corleis. The oxidising mixture used contained for each gram of aluminium: 15 c.c. of saturated copper sulphate solution, 15 c.c. of saturated chromium trioxide solution, and 60 c.c. of a mixture containing by volume 5 parts of saturated chromium trioxide solution, 75 parts of concentrated sulphuric acid, 20 parts of phosphoric acid, and 35 parts of water. Solution of the metal is rapid and may be too violent at first. CHEMICAL ABSTRACTS.

The Detection of Carbon Monoxide. C. R. HOOVER (*J. Ind. Eng. Chem.*, 1921, **13**, 770—772).—An absorbent, Hoolamite, (U.S. Pats. 1321061 and 1321062), is prepared by mixing together fuming sulphuric acid 53—56%, iodine pentoxide 10·6—12%, and pumice stone 33—35%. At ordinary temperatures carbon monoxide is oxidised by this reagent to carbon dioxide with liberation of iodine, which reacts with excess of sulphur trioxide present to form a green substance indicative of the presence of carbon monoxide, and varying in depth with concentration of the gas. On keeping or gentle warming the green colour changes to orange-yellow and disappears in a few minutes, so that the material can again be used as before until about twelve tests have been made, when the colour produced becomes irregular and a fresh supply of reagent is required. The colour produced in each case is compared with permanent colour standards prepared from a mixture of pumice granules with normal and basic copper acetate and chromium oxide. By this means a quantitative test can be made with gas mixtures containing up to 0·2% of carbon monoxide. Interfering gases such an unsaturated hydrocarbons, hydrogen sulphide, etc., are first removed from a gaseous mixture by passing it through dry active charcoal. 0·005% of carbon monoxide can be detected by passing 500 c.c. of a gas mixture through a glass tube containing a column of Hoolamite 50 mm. × 5 mm. A pocket size detector apparatus has been devised. S. S. A.

Estimation of Potassium in the Presence of Sodium, Magnesium, Sulphates, and Phosphates. H. ATKINSON (*Analyst*, 1921, **46**, 354—355).—The method depends on the solubility of sodium and magnesium perchlorates, sulphates, and

phosphates in methyl alcohol. The mixture of the salts is evaporated with perchloric acid until fumes of the latter are evolved, a further quantity of the acid is added and the evaporation repeated, and 100 c.c. of methyl alcohol are then added. The mixture is boiled for about one hour, cooled, and, after eighteen hours, the potassium perchlorate is collected on a filter, washed with 50 c.c. of methyl alcohol containing 5% by vol. of perchloric acid, *d* 1·12, and then with 20 c.c. of ethyl alcohol. W. P. S.

Estimation of Sodium, Potassium, Calcium, and Magnesium, in Urine, Blood, and Fæces. FREDERICK F. TISDALL and BENJAMIN KRAMER (*J. Biol. Chem.*, 1921, **48**, 1—12, and 223—232).—Rapid methods are described for the estimation of these metals in blood, urine, and fæces. The quantities of material required for the complete analysis are 7 c.c. of blood, 50 c.c. of urine, and 2 grams of dried fæces. C. R. H.

Methods of Estimating Calcium in the Blood. Experimental Control of the Methods of Jansen and of Marriott and Howland. H. LABBÉ and G. DE TONI (*J. Pharm. Chim.*, 1921, [vii], **24**, 247—255).—The titrimetric method of Jansen (A., 1918, ii, 174) gives results of which the accuracy is by no means proportional to the delicacy and length of the procedure. At least three estimations in each case are necessary in order to obtain a mean value closely approximating to the actual figure, and as each experiment requires 10 c.c. of blood, the amount required is fairly considerable, especially if dealing with children. The colorimetric method of Marriott and Howland (A., 1916, ii, 269; 1918, ii, 21), depending on the decolorisation of ferric thiocyanate by oxalates, is not sufficiently delicate, the variations in intensity of the colour being too slight and the readings therefore more or less arbitrary. The filtration of the minute quantities of calcium oxalate precipitate is also a weak point in the method and may lead to loss. G. F. M.

Behaviour of Ammonium Carbonate towards Magnessium. T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1921, **58**, 1250—1251).—In group analysis, addition of ammonium carbonate causes the precipitation of a double carbonate with magnesium if the solution is not sufficiently dilute. S. I. L.

A New Method for the Evaluation of Zinc Dust. BULLNHEIMER (*Metall u. Erz*, 1921, **18**, 443—446).—The dust is ground until it passes through a 90-mesh sieve; 1 gram is shaken with 20 c.c. of water in a 300 c.c. Erlenmeyer flask, 20 c.c. of sulphuric acid (100 grams per litre) and 25 c.c. of 3% hydrogen peroxide are then added together, and the whole is allowed to remain with occasional stirring for four to eight minutes. The zinc particles should then be all dissolved, leaving only a loose metallic slime of lead, etc. Twenty c.c. of 40% sulphuric acid are then added and the excess of hydrogen peroxide estimated by titration with potassium permanganate solution (15 grams per litre) which has been standardised against sodium oxalate. For exact results, the above

quantities and procedure must be strictly adhered to, the solution of the zinc must not take more than ten minutes and the titration must be carried out immediately after this. A. R. P.

Estimation of Small Quantities of Zinc. M. BODANSKY (*J. Ind. Eng. Chem.*, 1921, **13**, 696—697).—To estimate small quantities of zinc in foods, etc., a weighed portion of the substance is treated with sulphuric acid and nitric acid, incinerated, the ash dissolved in dilute hydrochloric acid, and the solution filtered and evaporated. The dry residue is dissolved in dilute hydrochloric acid, copper is removed as sulphide, and excess of hydrogen sulphide is expelled by boiling the solution; the latter is then neutralised with ammonia, treated with 10 c.c. of 50% citric acid solution, boiled, small quantities of calcium carbonate are added until a precipitate of about 1 gram of calcium citrate has formed and the mixture is treated with hydrogen sulphide. After some hours, the precipitate is collected, washed with 2% ammonium thiocyanate solution, dissolved in hot dilute hydrochloric acid, the solution diluted to 45 c.c. and treated with potassium ferrocyanide solution. The turbidity obtained is compared with that produced by a known amount of zinc under similar conditions. W. P. S.

Gravimetric Analysis. XIX. XXIV. Estimation of Cadmium. II. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1921, **34**, 466—467; cf. this vol., ii, 559).—The cadmium is precipitated as cadmium ammonium phosphate, $Cd(NH_4)PO_4,H_2O$, by the addition of a considerable excess of 20% diammonium hydrogen phosphate solution to a very faintly acid, hot, dilute solution of a cadmium salt containing about 2% of ammonium chloride. The precipitate, initially amorphous, becomes crystalline on keeping for an hour with occasional stirring, and after two hours, or the next morning if desired, it is collected, washed with 50 c.c. of cold, saturated cadmium ammonium phosphate solution, and finally with methyl alcohol, and dried for two hours at 100°, at which temperature the water of crystallisation is not lost. As a further check on the weight, the precipitate may be converted in the pyrophosphate by ignition in a platinum crucible. The corrections to be applied to the weight of $Cd(NH_4)PO_4,H_2O$ obtained are as follows: Weight of precipitate 0·2—0·3 gram, add 0·2 mg.; 0·1 gram, add 0·3 mg.; 0·05 gram, add 0·4 mg.; 0·01 gram, add 1·9 mg. The presence in moderate quantity of other ammonium salts, sodium or potassium chloride, etc., does not appreciably affect the accuracy of the estimation. G. F. M.

Rapid Estimation of Copper or Iron in Aluminium–Copper or Aluminium–Iron Alloys. PIERRE HULOT (*Bull. Soc. chim.*, 1921, [iv], **29**, 836—837).—Two to five grams of the alloy, according to the expected copper or iron content, are treated with cold 20% sodium or potassium hydroxide. The aluminium rapidly dissolves and the iron or copper is deposited. The metallic deposit is washed thoroughly by decantation, dried, and weighed. The results may be confirmed in the case of copper by dissolving the

deposit in nitric acid and estimating the copper electrolytically. In the case of iron, the metal is dissolved in hydrochloric acid and estimated in the usual way by precipitation as ferric hydroxide.
W. G.

The Estimation of Mercury in Organic Compounds. HUGO BAUER (*Ber.*, 1921, **54**, [*B*], 2079—2081).—The method consists in a modification of the procedure proposed by Rupp (A., 1908, ii, 1073) and by Wöber (A., 1920, ii, 333).

The substance (0·2—0·3 gram) is weighed into a wide-necked Jena glass flask provided with a two-holed rubber stopper carrying a small dropping funnel and a glass tube leading to a Peligot tube containing about 5 c.c. of water. Concentrated sulphuric acid (10 c.c.) is run into the flask (if the substance is in aqueous solution it is preferable to add fuming sulphuric acid) followed by hydrogen peroxide solution (30%, 3—5 c.c.), which is added slowly and with constant agitation and intermittent warming until a colourless solution is obtained; this operation is usually complete in a few minutes. The contents of the flask and Peligot tube are rinsed into a small beaker, and concentrated ammonia is added in slight excess, after which the mixture is covered and heated at its boiling point for about three minutes to destroy the Caro's acid formed. Ten c.c. of approximately *N*/5-potassium cyanide solution are added to the cooled mixture, followed by 5 drops of potassium iodide solution (10%). Excess of potassium cyanide is titrated with *N*/20 silver nitrate solution. The titre of the potassium cyanide solution must be determined daily by diluting 10 c.c. of it with water (30 c.c.) adding a few drops of ammonia and potassium iodide, and titrating with *N*/20-silver nitrate. H. W.

Estimation of Metallic Aluminium and of Aluminium Oxide in the Commercial Metal. JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1921, **13**, 808—812).—The metal is dissolved in sodium hydroxide or in acid in a special apparatus and the hydrogen liberated is collected in a measuring burette where its volume, temperature, and pressure may be read. The volume of gas is equivalent to unoxidised aluminium, together with whatever iron is present when an acid reagent is used, or with the silicon when sodium hydroxide is used. The amount of the oxide content is calculated by difference from the estimated total aluminium present.
S. S. A.

Separation of Aluminium from Glucinum. HUBERT T. S. BRITTON (*Analyst*, 1921, **46**, 359—366).—A solution of salts of the two metals, containing not more than 0·3 gram of glucina and 0·4 gram of alumina, is evaporated to a volume of about 25 c.c., cooled, and 24% sodium hydroxide solution is added in quantity just sufficient to re-dissolve the precipitated hydroxides. The mixture is then diluted to 500 c.c., boiled for forty minutes, the precipitated glucinum hydroxide collected on a filter, washed, ignited, and weighed. The filtrate is acidified with hydrochloric acid and the aluminium precipitated as hydroxide by the addition of ammonia. W. P. S.

Colorimetric Estimation of Iron in Silicates with Ammonium Thiocyanate. JOSEF MATEJKA (*Chem. Listy*, 1921, **15**, 8—13; cf. Thomson, T., 1885, **47**, 493).—One to 2 c.c. of a standard iron solution (containing ferrous iron equivalent to 0·01 gram of ferric oxide per litre of 0·5% sulphuric acid), 8 c.c. of a mixture of 1 part of 10% nitric acid with 3 parts of 10% citric acid solution by volume, and 8 c.c. of 10% ammonium thiocyanate solution are diluted to the 20 c.c. mark in a colorimetric tube. Two similar tubes contain similar quantities of the same solutions, with the exception of the iron, diluted to about 19 c.c. The solution of the pyrosulphate fusion of the silicate in 0·5% sulphuric acid, having been diluted to 250 c.c., is added drop by drop to one tube until equivalent coloration is attained; on repeating the process, it is necessary that the final volume in the tube should be exactly 20 c.c. It is essential that the thiocyanate should be present in excess, and that its concentration should be the same in both tubes (cf. Tatlock, A., 1888, 90). Potassium sulphate and potassium hydrogen sulphate cause a reduction of the intensity and change the colour from pink to orange. Sodium, magnesium, calcium, and titanium chlorides and aluminium salts have a detrimental effect. The interference of all these salts is, however, inappreciable if the solution to be tested is sufficiently acidified with nitric and citric acids before the addition of thiocyanate. The method is equally as satisfactory as that of Lunge (*Zeitsch. angew. Chem.*, 1886, 3). CHEMICAL ABSTRACTS.

A Simple, Exact, and Rapid Electrolytic Estimation of Cobalt in Ammoniacal Solution and its Application to Cobalt Nitroso-β-naphthol. K. WAGENMANN (*Metall u. Erz*, 1921, **18**, 447—449).—Cobalt may be rapidly and accurately deposited electrolytically on a rotating double platinum gauze cathode with a current of 5 amperes from a solution containing 5 grams of ammonium chloride, 30 c.c. of strong ammonia, and not more than 0·1 gram of cobalt as sulphate in a bulk of 125—150 c.c. In order to obtain bright, strongly adhering deposits, the cathode is rotated at 600—1200 revolutions per minute and 0·8—1·0 gram of hydrazine sulphate is added a little at a time during the electrolysis, which is complete in forty to forty-five minutes. Precipitation of cobalt with nitroso-β-naphthol and direct ignition of the precipitate to Co_3O_4 usually yields slightly high results due to inclusion of traces of iron, alumina, and copper, if present. The ignited oxide may be dissolved in fused alkali hydrogen sulphate, and the solution treated with ammonia and ammonium chloride and electrolysed as described above. A. R. P.

Volumetric Estimation of Tin with Potassium Bromate. V. VELICH (*Chem. Listy*, 1921, **15**, 5—8, 38—41, 56—59).—The method as proposed by Fichter and Müller (A., 1913, ii, 34) is more fully developed. The reduction of solutions of stannic chloride in preparation for titration is best conducted in a closed flask, provided with a Fresenius stopper, an inlet tube for the addition of liquids, and an inlet tube for the continuous passage of carbon

dioxide. Aluminium is the best reducing agent, but in the estimation of tin in alloys the presence of nickel during the reduction with aluminium aids materially. Metals which are precipitated during the aluminium reduction and do not redissolve in hydrochloric acid are removed by filtration through an asbestos mat under reduced pressure and in an atmosphere of carbon dioxide to prevent re-oxidation. It is best to use a 0·2*N*-solution of potassium bromate, kept in an atmosphere of carbon dioxide, for the titration. Various indicators (oxazines, thiazines, and azines) were tried. Capri-blue (L) is the most suitable for this reaction. The above method gives satisfactory results for the estimation of tin in relatively pure preparations and in alloys if these contain less than 0·3% of iron.

CHEMICAL ABSTRACTS.

Estimation of Vanadium in Ores and Metallurgical Products. R. B. SCHAAL (*J. Ind. Eng. Chem.*, 1921, **13**, 698—699).—From 1 to 5 grams of the ore are boiled with 60 c.c. of hydrochloric acid, 5 c.c. of nitric acid and 2 c.c. of hydrofluoric acid are then added and the mixture is evaporated to dryness; in the case of ferrovanadium, a similar procedure is used to obtain the metal in solution, but the hydrochloric acid is added after the other acids; steel is dissolved in hydrochloric acid and the solution evaporated with the addition of nitric acid. The residue obtained as described is twice evaporated with the addition of hydrochloric acid, then dissolved in hydrochloric acid, and the solution diluted and filtered. The filtrate is treated with 60 c.c. of 15% ammonium phosphate solution and ammonia is added until a precipitate of ferric phosphate is formed; the latter is dissolved in a slight excess of hydrochloric acid, the whole mixture is diluted to 300 c.c., and titrated with standard potassium permanganate solution. W. P. S.

Solidifying Rate of Paraffins. K. FRICKE (*Chem. Zeit.*, 1921, **45**, 891—892).—To ascertain the suitability of solid paraffins for candle-making, the author determines the solidifying rate or period required for a melted paraffin to form a mass sufficiently hard to support a given weight. One hundred grams of the paraffin are melted at 65° and poured into a metal dish, 11 by 6 cm. and 3·5 cm. in depth, and containing a thermometer. As soon as the first signs of solidification are noticed, the time is noted and after a further fifty-five minutes the lower end of an iron rod, 19 cm. square and weighing 205 grams, is placed on the surface of the paraffin 2·5 cm. from the side of the dish. The rod is supported vertically and carries a weight of 2 kilos. If the end of the rod sinks into the paraffin, the test is made again after five minutes, and so on, until the depression made by the rod is negligible. A suitable paraffin will solidify to this consistence within sixty-five minutes.

W. P. S.

Detection and Estimation of Coal-tar Oils in Turpentine. V. E. GROTLISCH and W. C. SMITH (*J. Ind. Eng. Chem.*, 1921, **13**, 791—793).—One hundred c.c. of the turpentine are saturated with hydrogen chloride at a low temperature, the pinene hydrochloride

formed is separated by filtration, and the filtrate is distilled under reduced pressure until about 25 c.c. of distillate have been obtained; any tar-oils (toluene, xylene, and commercial solvent naphtha) present are thus concentrated in this distillate. The latter is added slowly to 100 c.c. of sulphuric acid containing 4% of free sulphur trioxide, the mixture is then heated at 70° for twenty minutes, cooled, diluted with water, and distilled with steam. Pure turpentine yields about 0·5 c.c. of yellow oil, n_D^{20} above 1·500; if mineral oil is present it is recovered at this point and is identified by its odour. When oil ceases to distil, the steam supply is disconnected and the mixture distilled directly, warm water being added drop by drop at such a rate that the temperature of the mixture rises gradually. Hydrolysis of the sulphonated hydrocarbons commences at 115° and the free hydrocarbon distils; the distillation is stopped when the temperature approaches 170°. The volume of oil recovered in the distillate is multiplied by 2·2 to obtain the percentage amount of coal-tar oils in the sample, and these oils may be identified by the usual tests (nitration, etc.). The method is not trustworthy in the case of wood turpentines as the use of high temperatures in the distillation of the wood converts a portion of the terpenes into cyclic hydrocarbons. W. P. S.

Estimation of Volatile Alcohols. AD. GRÜN and TH. WIRTH (*Zeitsch. Deut. Oel-Fett. Ind.*, 1921, **41**, 145—147).—To 0·5 to 1 gram of the sample in a 100 c.c. flask are added 5—10 c.c. of lauryl chloride prepared by distilling a mixture of lauric acid with phosphorus trichloride or pentachloride. The flask is plugged with cotton-wool, kept at about 60° for one-half to three hours, the contents are then shaken with 50 c.c. of water, boiled for one minute, cooled, extracted with ether, the free lauric acid is neutralised, and the ester quantitatively hydrolysed with potassium hydroxide. Simple, readily volatile alcohols can be accurately estimated, but such substances as geraniol and methylnonylcarbinol require to be kept for three hours at 60°. Secondary alcohols the hydroxyl group of which is attached to a ring carbon atom, for example, menthol, and tertiary alcohols do not, however, yield satisfactory results.
CHEMICAL ABSTRACTS.

Estimation of Alcohols and Phenols in Ethereal Oils by Esterification with Pyridine. H. W. VAN URK (*Pharm. Weekblad*, 1921, **58**, 1265—1269).—Verley and Bölsing's method (A., 1902, ii, 54) has been examined for menthol, eugenol, and santal oils. In no case does the method give very exact results, but given conditions under which quick determinations may be made for santal oil and eugenol with fair approximation. S. I. L.

A Method for the Estimation of Sugar in Normal Urine. STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1921, **48**, 51—57; cf. also A., 1918, ii, 246).—By elimination, by the use of acetone, of the confusion due to the presence of creatinine, the picric acid method of sugar estimation of Lewis and Benedict (A., 1915, ii, 111) is made applicable to urine. The addition of acetone

destroys the colour produced by creatinine, whilst leaving unaffected that due to the sugar. C. R. H.

Estimation of Lactose in the Presence of other Reducing Sugars. L. LE GRAND (*Ann. Falsif.*, 1921, **14**, 268—269).—In using Barfoed's method (this vol., ii, 355) for the estimation of lactose in milk, the sugar solution should be diluted so that the concentration of alkali or alkaline-earth salts does not exceed 0·1%; when these salts are present in greater concentration, basic salts are precipitated and interfere with the estimation. W. P. S.

Revision of the Optical Method for Analysing Mixtures of Sucrose and Raffinose. C. A. BROWNE and C. A. GAMBLE (*J. Ind. Eng. Chem.*, 1921, **13**, 793—797).—Owing to the change in the Herzfeld divisor of the Clerget formula for estimating sucrose from 142·66 to 143, a revision of the Creydt formula for analysing mixtures of sucrose and raffinose is necessary. On the basis of the invert factor −0·33 for sucrose and +0·514 for raffinose, and 1·852 as the ratio of the specific rotation of sucrose to that of raffinose, the percentages of sucrose (S) and of raffinose (R) in a mixture are found by the formulæ: $S=0{\cdot}514, P-P'/0{\cdot}844$, and $R=0{\cdot}33\ P+P'/1{\cdot}563$, where P and P' are the direct and invert polarimetric readings at 20° of a normal (sucrose) weight solution of the mixture. General formulæ, applicable at all temperatures, are as follows: $S=P(0{\cdot}478\times 0{\cdot}0018t)-P'(1{\cdot}006-0{\cdot}0003T)/(0{\cdot}908-0{\cdot}0032t)(1{\cdot}006-0{\cdot}0003T)$ and $R=P(0{\cdot}43-0{\cdot}005t)+P'(1{\cdot}006-0{\cdot}0003T)/(1{\cdot}681-0{\cdot}0059t)(1{\cdot}006-0{\cdot}0003T)$, where T is the temperature of the direct polarisation and t that of the invert polarisation.
W. P. S.

The Use of Taka-diastase in Estimating Starch. EDWARD HORTON (*J. Agric. Sci.*, 1921, **11**, 240—257).—The results of much experimental work on the estimation of starch by hydrolysis with taka-diastase are recorded, and show that the method is not always trustworthy. The quantity of enzyme suggested in the original method (Davis and Daisch, A., 1914, ii, 588) seems insufficient. Various commercial samples of the enzyme gave unsatisfactory results, and samples were prepared by the growth of *Aspergillus oryzæ* on sterile bran and on Munter's medium. The activity of the enzyme so prepared increased until the seventh day of growth and then declined. The use of asparagine as the source of nitrogen in the medium tends to produce a more active enzyme. On the whole, laboratory prepared samples gave no better results than commercial ones. Discordant figures are obtained if different classifying agents are used previously to the final sugar estimation. The addition of malt diastase does not increase the total starch figure, but raises the ratio: dextrose/maltose. The cause of the unsatisfactory results is not clear, but although evidence is somewhat conflicting, the theory that it is due to the persistence of dextrins has the greater weight. Control experiments with the enzyme used should be made on pure starch with each set of estimations. Results on this basis are fairly trustworthy. A. G. P.

Precipitation of Solid Fatty Acids with Lead Acetate in Alcoholic Solution. E. TWITCHELL (*J. Ind. Eng. Chem.*, 1921, **13**, 806—807).—The following procedure is recommended for the estimation of solid fatty acids in a mixture of fatty acids. Ten grams of the fatty acids from an oil, or 2 grams of the fatty acids from a fat, are dissolved in 95% alcohol, the solution is boiled, and 1·5 grams of lead acetate dissolved in boiling alcohol are added; the total volume of alcohol used should be 100 c.c. The mixture is cooled slowly to 15°, and, after about eighteen hours, the precipitate is collected on a filter and washed with alcohol until the filtrate ceases to give a turbidity when diluted with water. The precipitate is now dissolved in 100 c.c. of boiling alcohol containing 0·5 c.c. of acetic acid, the solution cooled, and the precipitate again collected, washed, transferred to a separating funnel, and shaken with ether and nitric acid; the ethereal solution is separated, washed, evaporated, and the residue of fatty acids weighed. Fatty acids from different oils yielded the following quantities of solid fatty acids: Cotton-seed oil, 23·13%; soja bean oil, 17·01%; olive oil, 10·93%; earth-nut oil, 16·58%; lard, 40·02%; partly hydrogenated cotton-seed oil, 50·62%; tallow, 53·62%. The iodine value of the solid fatty acids was less than 1·0, except in the case of the hydrogenated cotton-seed oil (42·21) and the tallow (4·38). W. P. S.

Identification of Tartaric Acid in Wines. L. MATHIEU (*Ann. Falsif.*, 1921, **14**, 281—283).—Amyl alcohol extracts a portion of the free tartaric acid from wine, but not potassium hydrogen tartrate or calcium tartrate. Twenty c.c. of the wine are shaken with 20 c.c. of amyl alcohol, the latter is separated and shaken with 20 c.c. of water, and this aqueous extract is evaporated to dryness; the residue obtained is dissolved in 5 c.c. of water and the solution is treated with one drop of calcium chloride solution (15 grams of calcium chloride and 40 grams of ammonium chloride per litre) and 2 c.c. of *l*-ammonium tartrate solution. A precipitate of calcium racemate forms at once if the wine contained 0·5 gram, or more, of free tartaric acid per litre. W. P. S.

Rapid Method for the Estimation of Hippuric Acid in Urine. F. B. KINGSBURY and W. W. SWANSON (*J. Biol. Chem.*, 1921, **48**, 13—20).—The authors describe a modification of the method of Folin and Flanders (A., 1912, ii, 396, 501) for the estimation of hippuric acid, by which, without sacrificing accuracy, the time necessary for the estimation is reduced from nine hours to between two and three hours. C. R. H.

Determination of Watering and Creaming in Samples of Altered Milk. G. ANDOYER (*Comp. rend.*, 1921, **173**, 588—589).—It is shown that the coagulum of sour milk, when freed from fat and mineral matter, contains 15·6% of nitrogen. Thus the method of Kling and Roy for the analysis of samples of sour milk may be modified. The sample, after the addition of a little acetic acid, is filtered on a tared filter and washed with water. The coagulum is dried, extracted with ether, the fat being subsequently recovered and weighed, again dried, weighed, and incin-

erated. In the filtrate and washings the total ash and the soluble nitrogen are determined. From these data the percentages of fat, casein, and ash in the original milk can be calculated and any adulteration detected. W. G.

Detection of Formaldehyde by Resorcinol and Sulphuric Acid. ROBERT COHN (*Chem. Zeit.*, 1921, **45**, 997—998).—Krauss and Tampke's method (A., 1921, ii, 466) for the simultaneous detection of tartaric, oxalic, and formic acids by resorcinol and sulphuric acid has the disadvantage that the reaction is much more sensitive for the detection of tartaric acid than it is for the detection of oxalic or formic acid, and, consequently, it cannot always be applied for the detection of formic acid in food. In order to determine whether the formic acid reaction is influenced by the presence of other organic preservatives which are volatile with steam, the behaviour of formaldehyde with resorcinol and sulphuric acid was examined, and it was found that this reagent is very sensitive for the detection of formaldehyde. Two c.c. of 0·1% aqueous pure resorcinol solution are shaken with an equal volume of the distillate to be tested and about 2 c.c. of concentrated sulphuric acid are then added so as to form a layer below the solution. In the presence of formaldehyde a ring of white flocks with a violet-red coloured base is formed at the junction of the two liquids. After some time, the zone of white flocks increases upwards and a red precipitate, insoluble in water, separates. The reaction is immediate when the solution contains 0·01 gram of formaldehyde per 100 c.c., and is still distinct with only 0·05 mg. of formaldehyde. In the latter case, the violet-red ring may be faint, but the separation of the characteristic white flocks, which increase in quantity on keeping, is distinct. In presence of formic acid, oxalic acid, and tartaric acid, the ring of white flocks with a violet-red coloured base is formed first, although the violet-red colour may be masked by the brown formic acid ring; below this is the blue oxalic acid ring, and when the lower part of the tube is heated carefully, the deep red tartaric acid ring is formed at the bottom. When the test is carried out as described above with other aldehydes or their derivatives, a characteristic zone of white flocks is also produced, but a different coloured ring is formed at its base. Thus, benzaldehyde gives an intense yellow, acetaldehyde deep green, hexamethylenetetramine greenish-brown, and dilute furfuraldehyde solution black-violet. F. M. R.

Separation of Aliphatic Amines from one another and from Ammonia. HARTWIG FRANZEN and ARTUR SCHNEIDER (*Biochem. Zeitsch.*, 1921, **116**, 195—207).—For the investigation of the volatile bases of plants, a method for their quantitative separation is necessary. This can be effected as follows. Ammonium chloride and monomethylamine hydrochloride are insoluble in chloroform, whilst the hydrochlorides of di- and tri-methylamines are soluble. The ammonia and monomethylamine can be separated by addition of yellow mercuric oxide, which, provided the ammonia be not greatly in excess of the methylamine, combines with ammonia

alone. Di- and tri-methylamines can be separated by treatment with iodine in potassium iodide solution, which precipitates the trimethylamine as periodide. H. K.

Behaviour of Nevralteine with Quinine Salts : Easy Method for its Identification. MARIO CARDINI (*Boll. Chim. Farm.*, 1921, **60**, 253—258).—The following reaction has been tested with all the antipyretics at present in use, and is found to be given only by nevralteine (sodium *p*-phenetidinomethanesulphonate) : A small quantity (0·02 gram) of the substance and 0·01 gram of quinine hydrochloride or sulphate are treated together in a porcelain dish with a drop of water, a characteristic reddish-yellow coloration being obtained with nevralteine. T. H. P.

Rapid Estimation of Carbamide in Urine, Blood, and other Physiological Fluids. H. STROHMANN and S. FLINTZER (*Zentr. inn. Med.*, 1921, **42**, 545—562; from *Chem. Zentr.*, 1921, iv, 493—494).—An examination of the methods of Folin and his co-workers (A., 1919, ii, 308). Difficulties in the hydrolysis by means of urease may be avoided by using smaller amounts of material (= about 0·2 gram of carbamide nitrogen) and working at greater dilutions. On account of the errors consequent on the small amounts of nitrogen to be estimated, the older method of Marshall (A., 1913, ii, 640) was tried. It gave more concordant results but demanded longer time. Using 10 c.c. of blood filtrate (instead of 5 c.c. as in Folin's method), the liquid may be nesslerised directly after hydrolysis if the same amount of ferment extract is added to the liquid used for comparison. The method to be adopted for the preliminary removal of protein will vary according to the liquid under examination and the amount of protein present. G. W. R.

Typical Reaction for the Differentiation of Carbazole Derivatives. A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 625).—A number of examples are quoted to show that the colour developed on the addition of nitric acid to a solution of a derivative of carbazole is characteristic, and serves as an excellent criterion of purity. J. K.

Comparison of Methods for Estimation of Uric Acid in Blood. PIETRO BIFFI (*Riv. osp.*, 11, 29—40; from *Chem. Zentr.*, 1921, iv, 493).—The methods of Ludwig-Salkowski, Schittenhelm-Schneller, Kowarski (piperidine), and Aufrecht (hydroxyl estimation of ammonium urate) for the estimation of uric acid in blood were compared in cases of pathological bloods. The agreement was unsatisfactory, but the first two gave the most concordant results. The second method would appear to be the most trustworthy. A modification of the Kowarski method (precipitation of the proteins by sulphosalicylic acid, transformation by means of ammonium chloride into ammonium urate, and, after washing with ethyl alcohol–acetone, estimation of the ammonia) gave passable results, but was less accurate than the methods first named. G. W. R.

General and Physical Chemistry.

Refractive Indices of Mercury and Thallium Vapours. J. C. McLennan (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 191—200).—The refractive indices of mercury and thallium vapour have been determined for a number of wave-lengths both by the prism method and the interferometer method. A method is described by which interferometer tubes and hollow prisms of clear fused quartz, free from distortion and all trace of devitrification, can be made. These instruments were employed in the present experiments and found to yield satisfactory results. The dispersion curve for non-luminous thallium vapour indicates the existence of anomalous dispersion at the wave-lengths $\lambda\lambda$ 5350·65 and 6000 Å.U. The following values of the refractive index were obtained: mercury vapour at normal pressure and temperature by the interferometer method, λ 4860, μ_0 1·000949; λ 5132, μ_0 1·000943; λ 6110, μ_0 1·000924; λ 6230, μ_0 1·000882; prism method, λ 4358·56, μ_0 1·000942; λ 5460·97, μ_0 1·000902; λ 5780, μ_0 1·000891; λ 6234·31, μ_0 1·000860: thallium vapour at 540°, λ 4358·56; μ 1·000229, λ 4861·49, μ 1·000110; λ 5460·97, μ 1·000293; λ 5769·45, μ 1·000222; λ 5790·49, μ 1·000144; λ 5893, 1·000165; λ 6234·31, μ 1·000309; λ 6563·04, μ 1·000142. J. F. S.

Hydrogen Spectra from Long Vacuum Tubes. R. W. Wood (*Phil. Mag.*, 1921, [vi], **42**, 729—745; cf. A., 1920, ii, 569).—A continuation of previous work (*loc. cit.*). It is shown that in a tube of great length (190 cm.), containing hydrogen with a suitable trace of water-vapour, the centre of the tube exhibits the Balmer series with the secondary spectrum reduced to 1/50 of its usual intensity. The ends of the tube (to a distance of about 40 cm. from the electrode bulbs) show the secondary spectrum strongly developed in addition to the Balmer series. The phenomena are of the same nature with a continuous current of high potential as with an alternating current; that is, the secondary spectrum develops at both the anode and cathode. With the tube in this condition, the central portion shows a bright flash of the secondary spectrum on closing the switch; the duration of this flash is about 1/50 sec.; on opening the switch the gas recovers its initial condition in about 1/5 sec. and shows the flash again on closing the switch. The secondary spectrum is attributed to molecular hydrogen by Merton, Stark, and others. The first rush of the current appears to break down the molecular hydrogen with the emission of a flash, leaving only atomic hydrogen in the centre of the tube (which gives the Balmer lines). On stopping the current, molecular hydrogen is reformed in about 1/5 sec. The breakdown, however, requires the presence of a trace of water-vapour. A very weak current produces a fairly strong secondary spectrum in the centre

of the tube with the Balmer lines weak or absent. Increase of current weakens the secondary spectrum, which passes through a minimum of intensity as the current becomes stronger and at the same time the Balmer lines increase in intensity. This is probably explained by the fact that molecular hydrogen is reformed as rapidly as it is broken down by a weak current. As the current strength increases the proportion of atomic hydrogen becomes greater with weakening of the secondary spectrum and augmentation of the Balmer lines. This, however, does not go on indefinitely, for with a further increase of current beyond a definite value both spectra increase in intensity at about the same rate. In any case, the percentage of molecular hydrogen cannot be reduced below a certain minimum value. With dry hydrogen and the tube thoroughly free from water-vapour, the Balmer lines disappear entirely from the entire tube (with the exception of a faint trace of H_α). In this stage, a strong group of lines appears in the ultra-violet between the 4th and 5th Balmer lines. When the tube is in this, the white stage, operation with condenser discharges gives a red discharge which shows strongly developed Balmer lines, indicating that momentary currents of several thousand amperes are able to break up molecular hydrogen even in the absence of water-vapour.

J. F. S.

Structure of the Balmer Series Lines of Hydrogen. J. C. McLennan and P. Lowe (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 217—226).—The structure of the Balmer series of hydrogen lines has been examined, using a long discharge tube of the type recently introduced by Wood (A., 1920, ii, 569). The following doublet separations were found for the first four members of the Balmer series, H_α=0·154 Å.U., H_β=0·085 Å.U., H_γ=0·062 Å.U., and H_δ= 0·049 Å.U. When these separations are plotted against the squares of the corresponding wave-lengths they are shown to lie on a curve which points to the vanishing of the doublet separation at the short wave-length limit of the Balmer series. The lines H_α, H_β, H_γ, and H_δ have been shown to consist of triplets when the electric discharge takes place in hydrogen containing a trace of nitrogen. Experiments made to decide whether the third members of the triplets had their origin in the radiations emitted by nitrogen atoms or in a modification produced by the nitrogen in the radiations emitted by the atoms of hydrogen were not decisive.

J. F. S.

The Balmer Series of Hydrogen, and the Quantum Theory of Line Spectra. Raymond T. Birge (*Physical Rev.*, 1921, **17**, 589—607).—To make as accurate a comparison as possible between the best experimental results for the Balmer series of hydrogen and the theoretical results to be expected according to the latest developments of the quantum theory of line spectra, the experimental data are reviewed and the quantum theory of line spectra, as applied to the Balmer series, is summarised historically. The fine structure of H_α (λ=6563Å) consists of six lines, two of which

are relatively intense, and the author shows that Merton's measurements (A., 1920, ii, 457) of the separation, half-width and relative intensities of the H_α and H_β doublets accord with values derived from the recent Bohr-Kramers developments of the quantum theory, if a general field of 100 volts per cm. is assumed. A discussion of spectral formulæ for the Balmer series indicates (1) that the Rydberg number is not constant for different lines, (2) that this discrepancy between observed and computed results is somewhat reduced by the application of relativity mechanics, and (3) that the discrepancy is obliterated when account is taken of the fine structure of the lines. The Rydberg constant for hydrogen is then calculated to be 106,977·7±0·2 and the Rydberg spectral series constant for a nucleus of infinite mass is computed to be 109,736±0·2. A discussion of observations in mixtures of hydrogen and helium made by Merton and Nicholson (A., 1920, ii, 69) at relatively high pressures concludes the paper. The well known neutral effect of helium on neighbouring electrons together with the Maxwellian distribution of velocities, separations, etc., is quite sufficient to account for the experimental results thus far obtained.

CHEMICAL ABSTRACTS.

Temperature and Band Spectra. W. STEUBING (*Physikal. Zeitsch.*, 1921, **22**, 507—511).—The band spectrum of iodine vapour has been examined in the positive column of a discharge tube at a series of temperatures. The light of the positive column presents at ordinary external temperatures a yellowish-green colour, but as the temperature is raised this passes into a bluish-violet colour. Spectroscopically, it is found that as the temperature is raised the band spectrum diminishes in intensity, at first in the green and then gradually right across the spectrum to the orange, which is observed at 450°, the limit of the experiment. At the same time, the intensity of the continuous spectrum increases, so that it becomes responsible for the bluish-violet colour of the positive column. The loss of intensity of the band spectrum is accompanied by the appearance of a number of lines which become more intensive the more the spectrum loses its characteristic band appearance.

J. F. S.

Spectrum of Ionised Potassium. J. C. MCLENNAN (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 182—190).—The author has photographed the " ground spectrum " of potassium, using electrodeless tubes in which to excite the vapour. The wave-lengths obtained contain the values of 150 lines which were not found by Schillinger (A., 1910, ii, 369), for which an accuracy of 0·5 Å.U. is claimed. In photographing the spectrum with a vacuum spectrograph, wave-lengths were recorded at λλ 1742·2, 1493·4, 1395·4, 1199·7, 1135·0, and 1085·3 Å.U.; of these the first may possibly belong to potassium. The remaining five were also found in the helium spectrum, and may be due to atoms of mercury from diffusion from the pump. The wave-lengths of the enhanced spectrum of potassium, from the point of view of numbers and intensity, fall roughly into two divisions

with a certain amount of overlapping. In one division, the "optical" or "spectral" centre of gravity is approximately at λ=3800 Å.U., and in the other it is in the neighbourhood of λ= 2100 Å.U. This suggests a similarity with the ordinary and enhanced spectra of argon, the one with its centre of gravity at 3800 Å.U. corresponding with the red spectrum of argon, and the other to the blue spectrum of this element. J. F. S.

The Electrodeless Discharge in Sodium Vapour. JOHN K. ROBERTSON (*Nature*, 1921, **107**, 269).—A brilliant electrodeless discharge is obtained at a temperature of about 300° when a primary Tesla coil is placed about a highly exhausted pyrex bulb containing metallic sodium, and the whole enclosed in an oven. In addition to the *D*-lines, doublets at 6162 (and 6158), 5688 (and 5683), 4667, and 4497 may be observed, as well as faint probable doublets at 5153, 4980, and 4572. A. A. E.

Emission and Adsorption Spectra of Mercury. J. C. McLENNAN and W. W. SHAVER (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 200—217).—Using plates stained with dicyanin, the spectra of a number of elements have been photographed in the infra-red region. In the case of mercury, the spectrum was photographed up to λ 11137 Å.U. By the photographic method, as well as by the use of thalofide cells, it has been shown that non-luminous mercury vapour does not absorb radiation of the wave-length λ 10140 Å.U. It has been found that slight and scarcely visible deposits of mercury vapour markedly absorb radiation of the wave-length λ=10140 Å.U., and this result may possibly afford an explanation of the observations made by Dearle (A., 1916, ii, 590; 1919, ii, 126). By the use of thalofide cells (Case, *Physical Rev.*, 1920, 289) and low-intensity mercury arcs, it has been shown that radiation of the wave-length λ=10140 Å.U. may be strongly absorbed by luminous mercury vapour. From the absence of absorption of radiation of wave-length λ 10140 Å.U. by non-luminous mercury vapour, it follows that the atoms of mercury in their ordinary state do not possess a resonance potential of 1·26 volts, corresponding with λ 10140 Å.U., in addition to the well-established one of 4·9 volts, corresponding with λ 2536·72 Å.U. J. F. S.

Revision of Series in the Arc Spectrum of Mercury. HERBERT DINGLE (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 167—181).—The arc spectrum of mercury has been reinvestigated and the lines have been grouped in principal, sharp, diffuse, and fundamental series of quadruplets, a singlet series, and combination lines. Photographs and diagrams of the spectrum are included in the paper. The measurements were all made with a quartz Littrow spectrograph giving a dispersion of 7·9 Å.U. per mm. at λ 2400 and 12·9 Å.U. at λ 2800 and the values, given in the international scale, are claimed to be accurate to 0·03 Å.U. or less. J. F. S.

Anomalous Zeeman Effect and Series System for Neon and Mercury. A. LANDÉ (*Physikal. Zeitsch.*, 1921, **22**, 417—422).—The results of the quantum theoretical analysis of the terms of the Zeeman lines are collected and put forward as spectral combination, polarisation, and intensity rules. The complete series systems of neon and mercury are arranged by means of a principle of selection, of the nature of Sommerfeld's conception of the complete doublets and triplets, and from the arrangement, by means of the rules devised from previous work, the Zeeman type of each series is obtained. The agreement with experimental results as to the number, position, and intensity of the Zeeman components confirms the relationship, between the type separated by a magnetic field and the multiplication of lines without a field, which has been previously deduced on the basis of the quantum hypothesis. J. F. S.

The Electronic Structure of the Heavy Atoms and of their Spectral Lines. A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 647—649).—The method used in the detailed study of the *L*-series of uranium (cf. this vol., ii, 532) has been extended to gold, platinum, iridium, osmium, and tungsten. The variations of certain homologous rays have been followed and six new rays have been isolated. The wave-lengths of the *L*-rays of the elements tungsten to uranium are tabulated. W. G.

The Normal Orbit of the Electron in the Atom of Mercury. A. TERENIN (*Nature*, 1921, **107**, 203).—A photographic method of examining absorption by non-luminous mercury vapour up to λ 11300 Å.U. revealed the absence of a marked absorption at λ 10140, although the pressure of mercury vapour reached one atmosphere. Thus the postulation by Dearle of a second normal orbit in the mercury atom, of which the corresponding ionisation and resonance potentials have never been observed, is unnecessary. A. A. E.

Absorption of Light by Electrically Luminescent Mercury Vapour. E. P. METCALFE and B. VENKATESACHAR (*Proc. Roy. Soc.*, 1921, [*A*], **100**, 149—166).—Experiments are described in which mercury vapour at low pressures, rendered luminous by the passage of small electric currents, is found to exert powerful selective absorption. It is found that, of the series lines, those belonging to the first and second subordinate series of triplets exhibit heavy absorption. The following lines are absorbed: λλ (5461, 4359, 4047), 3342, (3663, 3132, 2967), 5289, 5295, 5308, 3655, 3650, 3126 Å.U. Photometric observations are recorded on the absorption and emission of λ 5461 Å.U. by columns of mercury-vapour of different lengths and carrying different currents. The relation between the ratio (emission/absorption) and the current density is found to be linear. The applicability of the Stewart-Kirchhoff law to bright line radiation is discussed, and it is shown

that the complexity of a line may have a great influence on its absorption. The lines 5461 Å.U. and 4359 A.U. have been reversed, so as to appear as dark lines on the white light spectrum of a carbon arc and the sun. The reversal of 5461 Å.U. has been studied in detail with a Fabry and Perot étalon and with an échelon spectroscope. J. F. S.

Permanganate Absorption Spectrum : Claim for Priority : Formula for Calculating the Uranium Spectrum. JAMES MOIR (*Trans. Roy. Soc. Sth. Africa*, 1921, **10**, 33—34).—The author claims priority for a formula giving the wave-lengths of the bands of permanganates (A., 1920, ii, 573) over Adinolfi (A., 1920, ii, 721). The formulæ put forward by the two authors differ in form, but reduce to the same expression. From the formula for the absorption spectrum of uranyl salts, $n=1/\lambda=2113+66N$, where $N=0$, 1, 2, 3, or 4 (*loc. cit.*), it is now shown that the bands of non-ionised solid salts may be calculated. Thus the bands of autunite are given by dividing the figures calculated by the above formula by the sixth root of the ratio of the molecular weight of the salt to that of UO_2^{++}. In this case the observed bands are λλ 1945, 2000, 2062, 2128, and 2190, whilst the bands calculated by the formula $n=1/\lambda=(2113+66N)/\sqrt[6]{914/2\times270}=1937+60{\cdot}5N$ are λλ 1937, 1997, 2058, 2118, and 2179. J. F. S.

Two Peculiar Luminescence [Phenomena]. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1921, **21**, 45—65).—On illuminating certain preparations of zinc oxide with ultra-violet rays, a luminescence is displayed which slowly increases in intensity to a maximum, and on removing the exciting rays immediately disappears, but a dark, fading period must be present. A weak and transient phosphorescence is shown at the same time. Several liquids when mixed with this variety of zinc oxide display marked constitutive actions on the intensity of the luminescence. When potassium iodide is moistened with 2—5*N*-hydrochloric acid, it emits a luminescence which lasts for about one second and may be photographed. The wave-length of the luminescence waves lies in the region 300—313 $\mu\mu$. A similar effect may be produced by partly substituting for hydrochloric acid potassium chloride, bromide or iodide, or ethyl alcohol. The optimum mixtures have been determined in each case. Potassium iodide becomes at first more active by the absorption of water-vapour and then much weaker. The optimum effect is observed with a vapour pressure of water of 14·6 mm. at 25°. Inactive preparations are rendered feebly active by absorption of moisture. The phenomenon in all probability depends on a crystallo-luminescence brought about by the potassium chloride. J. F. S.

Decomposition of Hydrogen Peroxide in Ultra-violet Light. GERTRUD KORNFELD (*Zeitsch. wiss. Photochem.*, 1921, **21**, 66—99).—Earlier measurements of the decomposition of hydrogen peroxide by ultra-violet light have shown that the Einstein equivalent law does

not hold for these cases, and further that the velocity of the process is dependent only on the quantity of light absorbed, and not on the concentration of the solution. The present work has as its object the investigation of the above-mentioned points. A series of measurements with non-homogeneous light of unknown wavelength was first made and found to be in keeping with the earlier work, since the velocity of the change is strongly reduced by small additions of acid or alkali. It was also found that a slight dependence of the reaction velocity on the concentration of the peroxide exists. The later experiments were made with light of wavelength 305—316 $\mu\mu$, and in each case the absorption was determined exactly. It is found that with increasing dilution the velocity is increasingly dependent on the concentration; the addition of acid also causes a diminution of the velocity which depends on the amount of acid added. That Einstein's equivalent law does not hold was confirmed, and it is shown that in the most favourable case I $h\nu$ brings about the decomposition of eighty molecules. Assumptions are made as to the mechanism of the process, and these lead to calculated results which agree with the experimental results. J. F. S.

Artificial Disintegration of Light Elements. (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1921, [vi], **42**, 809—825).—In previous papers (A., 1919, ii, 256—261; 1920, ii, 541) it was shown that when α-particles were passed through nitrogen, positively charged hydrogen atoms were liberated at high velocities, but an uncertainty remained as to the range of the hydrogen particle. With a new and improved microscope, the authors have now been able to show that the hydrogen particles emitted from nitrogen have a maximum range of 40 cm. of air, whereas the hydrogen particles from gaseous hydrogen or hydrogen compounds have a maximum range of 29 cm. of air, both being produced by α-particles from Radium-*C* of range 7 cm. of air. This proves definitely that the charged hydrogen particles do not come from either gaseous hydrogen or hydrogen compounds present as impurity in the nitrogen. The elements lithium, glucinum, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, and sulphur or a suitable compound have been treated with α-rays from a quantity of Radium-*C* equivalent to 20 mg. of radium at a distance of 3·5 cm. from the zinc sulphide screen. The number of scintillations per minute per mg. activity of the source has been determined at an absorption of 32 cm. of air. It is found that boron, nitrogen, fluorine, sodium, aluminium, and phosphorus give off charged hydrogen atoms with ranges in cm. of air, of *ca.* 45, 40, *ca.* 40, *ca.* 42, 90, and *ca.* 65 cm. respectively. Chlorine, calcium, titanium, manganese, iron, copper, tin, silver, and gold give no particles of a greater range than 32 cm. of air, but no investigation has been made for particles of a range less than 32 cm. of air. In the case of nitrogen, it is shown that the number of particles emitted increases rapidly with the velocity of the α-particles. In the case of aluminium, it is found that the

direction of escape of the particles is to a large extent independent of the direction of the impinging α-particles, nearly as many being expelled in the backward as in the forward direction. The range of the backward particles is less than that of the forward particles; for example, with α-particles of range 7·0 cm. of air, the maximum range is 67 cm. of air for the backward particles but 90 cm. for the forward particles. It is shown that only those elements with an atomic mass of $4n+2$ or $4n+3$, where n is a whole number, give rise to hydrogen atoms. This result is explicable on the hypothesis that these elements are built up from helium and hydrogen nuclei. To account for the liberation of a hydrogen atom at high speed, it is necessary to suppose that the hydrogen nuclei are satellites of the main nucleus. In a close collision, the α-particle is able to give sufficient energy to the satellite to cause its escape at high speed from the central nucleus. The velocity of escape of the hydrogen atom does not seem to be very closely connected with the nuclear charge of the disintegrated element, for the range of the hydrogen atoms from boron (charge 5) is greater than that for nitrogen (charge 7), whilst the range of the hydrogen atom from aluminium (13) is greater than that from phosphorus (14). The above hypothesis assumes that positively charged substances attract one another at the very small distances involved. Such attractive forces must exist to hold the ordinary composite nucleus in equilibrium, and it seems likely that these attractive forces will extend some distance from the nucleus. If this view is correct, the forces on the α-particle are initially repulsive, but change sign very near the nucleus. Hydrogen atoms do not appear to be liberated from aluminium by α-particles of less range than 5 cm. This and the increased number liberated by an increase in the velocity of the α-particle shows that the "disruption" potential of the nucleus by an α-particle, that is, the potential difference required to communicate the same energy to an electron as is possessed by the α-particle, is of the order of six million volts for aluminium. J. F. S.

Production of Radiation and Ionisation by Electron Bombardment in Pure and in Impure Helium. Frank Horton and Ann Catherine Davies (*Phil. Mag.*, 1921, [vi], **42**, 746—773).—An outline of the development of ideas concerning the arrangement of the two electrons in the helium atom is given, starting with the author's determination of the minimum radiation voltage and the minimum ionisation voltage for normal helium (A., 1919, ii, 210). In this connexion, the theoretical deductions of Bohr, Franck, and Reiche (A., 1920, ii, 656), Landé (A., 1919, ii, 309), and Kemble (this vol., ii, 478) are discussed and the experimental work of Compton (A., 1920, ii, 725) and of Franck and Knipping (A., 1920, ii, 72) is considered and criticised. Because of the divergence in the results of the various investigators, the authors' former conclusions have been re-investigated, in a specially designed apparatus, over a wider range of pressures than used before. The new experiments show that in pure helium radiation is produced

by the impacts of electrons with 20·4 volts energy, in confirmation of the authors' earlier conclusions, but in disagreement with the most recent conclusions of Franck and Knipping. A second type of radiation is produced at 21·2 volts, in agreement with Franck and Knipping. The 21·2 volt radiation ionises abnormal helium produced by 20·4 volts electron impacts, and with a relatively high gas pressure the detected effects of ionisation may swamp those of radiation. This result provides an explanation of the ionisation of helium by electrons having less than the normal ionising velocity, which is essentially different from that offered by Compton. Both types of radiation can be absorbed and subsequently re-emitted by normal helium atoms, so that they are passed from atom to atom throughout a volume of the gas. For velocities below the normal ionising velocity, the amount of ionisation produced as the result of electron impacts on abnormal helium atoms, under the experimental conditions, is small in comparison with that resulting from the ionising action of the 21·2 volts radiation. The possibility of the presence of a small quantity of impurity in the helium facilitating the production of radiation at 20·4 volts has been investigated, but no evidence that impurity acts in this way has been obtained. It is concluded that the significance of the experimental results in connexion with theories of the arrangement of the two electrons in the normal helium atom lies in the fact that they indicate that the limitations of the selection principle are not applicable to the fundamental displacements of the outer electron of the helium atom. J. F. S.

***J*-Radiation.** J. A. CROWTHER (*Phil. Mag.*, 1921, [vi], **42**, 719—728).—The author has investigated the relative absorbability of the primary and secondary *X*-radiations from an aluminium radiator. It is shown that the ratio of the secondary radiation to primary radiation steadily diminishes as the thickness of the absorbing screens is increased. This indicates that the secondary radiation is distinctly more absorbable than the primary. The coefficients of absorption of primary and secondary fluorescent radiations in aluminium have been determined for the radiators paraffin wax, aluminium, and copper. The author shows that the *J*-radiation, unlike the *K*-radiation, consists, not of a group of lines of approximately the same wave-length, but of a considerable number of lines comparatively widely spaced in the spectrum. The *J*-radiations from elements of low atomic number are very weak compared with the *K*-radiations. In the case of copper, the intensity of the hard, fluorescent radiation is about 1/30 of that of the characteristic radiation from the radiator. This indicates that these hard, fluorescent radiations are not easily excited. To excite any given line of the series it is probably necessary that the wave-length of the primary radiation should not be much shorter than that of the line to be excited. The hard secondary radiations produced from aluminium, copper, and paraffin wax probably correspond with different lines in the *J*-spectrum of the elements.

J. F. S.

Explanation of Röntgen Spectra and the Constitution of the Atom. L. VEGARD (*Physikal. Zeitsch.*, 1921, **22**, 271—274), ADOLF SMEKAL (*ibid.*, 400—402).—Polemical. In the first paper Vegard replies to Smekal's criticism (A., 1920, ii, 654) of his theories on Röntgen spectra and the constitution of the atom (A., 1919, ii, 129). In the second paper Smekal maintains his earlier position.

J. F. S.

Wave-length of *X*-Rays. RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1921, **11**, 366—373).—A theoretical paper in which it is shown that with the existing knowledge it is impossible to determine definitely the structure of any crystal in advance of a knowledge of the wave-length of *X*-rays. Viewed from this position alone, the problem of the length of *X*-ray waves and of the structures of crystals becomes indeterminate. If the case of sodium chloride be taken as typical, it is shown that there are other structures, beside the commonly-accepted "sodium chloride arrangement," which are in agreement with the present experimental data. As a result of this lack of definiteness, it is emphasised that it is more logical to consider the value of the wave-lengths of *X*-rays as based on the quantum hypothesis. J. F. S.

The Mass Absorption and Mass Scattering Coefficients for Homogeneous *X*-Rays of Wave-length between 0·13 and 1·05 Ångström Units in Water, Lithium, Carbon, Nitrogen, Oxygen, Aluminium, and Iron. C. W. HEWLETT (*Physical Rev.*, 1921, **17**, 284—301).—The presentation of new experimental work is preceded by a discussion of the current views of the mechanism of absorption and scattering. The total absorption coefficient of homogeneous *X*-rays, obtained by means of a Bragg spectrometer, was measured for the above-named materials at various wave-lengths. The total mass absorption coefficient was found to be proportional to the cube of the wave-length over certain regions, but in all cases where the above range was entirely covered, the constant of proportionality differed for different ranges of wave-length. The case of hydrogen seems to be an exception, as its total mass coefficient was found proportional to the 9/2 power of the wave-length. This, however, was obtained by combining the results from water and liquid oxygen. The constant with which the cube of the wave-length is multiplied to give the true mass absorption coefficient is found to be approximately proportional to the cube of the atomic number of the absorbing element, except for lithium, indicating that Moseley's law does not hold for that element. The true mass absorption coefficient for iron is apparently not proportional to the cube of the wave-length between 0·70 and 1·05 Å.U. For other elements with wave-lengths less than 0·20 Å.U., these coefficients are smaller than is to be expected from theory if the electron has a diameter of the order of 10^{-13} cm. The lack of this decrease in the coefficients of iron is attributed to a shrinkage in the diameter of the electrons in the atoms on account of a closer packing of the electrons. The mass scattering coefficient

of all the materials studied is less than that given by Thomson's theory. For hydrogen it is approximately twice that for other elements, which is further evidence that hydrogen has twice as many scattering electrons per unit of mass as other elements. For iron this coefficient apparently increases for wave-lengths longer than 0·70 Å.U. CHEMICAL ABSTRACTS.

A Radioactive Quantity requiring a Name. N. ERNEST DORSEY (*J. Washington Acad. Sci.*, 1921, **11**, 381—386).—The author puts forward reasons for introducing a new radioactive quantity. The main reason is to avoid the use of long sentences in expressing the quantity of a radioactive substance used, such as "Radium-*C* corresponding with 1 gram radium." The quantity which the author terms "*r*" is that amount of the material which will produce transformed atoms at the same rate as transformed atoms are produced by 1 gram of radium. The author proposes that either the present definition of the curie be modified to meet the case, or a new unit, termed the *rutherford*, be introduced.

J. F. S.

Application of Anode Rays to the Investigation of Isotopes. G. P. THOMSON (*Phil. Mag.*, 1921, [vi], **42**, 857—867; cf. *Proc. Camb. Phil. Soc.*, xx, 210).—Photographs have been obtained for anode rays showing parabolas corresponding with singly charged atoms of lithium, glucinum, sodium, potassium, calcium, and strontium. Lithium is a mixture of isotopes of atomic weights 6 and 7. The proportions in which these appear in the rays are not constant, there being a tendency for the line at 6 to be sometimes considerably stronger than would be expected from the atomic weight. Glucinum is apparently single, atomic weight 9. If there is an isotope at 10 or 11, it is present in extremely small proportion. The remaining elements could not be resolved with the apparatus used, but calcium must consist of atoms of weight equal to those of either potassium or argon, that is, a so-called "isobar." No trace was found of doubly-charged metallic atoms or of atoms with a negative charge. It seems probable that the mechanism of the anode rays is more analogous to spluttering than to electrolysis. J. F. S.

Branching Relationship for Ra-*C*, Ac-*C*, Th-*C*, and the Disintegration Constant of the *C*″ Products. ELEONORE ALBRECHT (*Chem. Zentr.*, 1921, iii, 516; from *Sitzungsber. K. Akad. Wiss. Wien*, 1919, [2A], **128**, 925—944).—Making use of Marsden and Darwin's (A., 1912, ii, 824) relationship Th-C'' : Th-C=0·35, the author has determined the corresponding branch relationship for Ac-C and Ra-C. The C'' products were obtained by the recoil method from very active C products. From the electrometric measurements, the half life (T) has been calculated and the following values have been obtained, Ac-C'', T=4·76 min., Th-C'', T=3·20 min., and Ra-C'', T=1·32 min. The C'' products were collected on a negatively charged brass disk, which was placed above and very close to another plate containing the C products. A residual

activity, which is due to a contamination of the C'' plates by Ac($B+C$), Th($B+C$), or Ra-C respectively, is estimated and brought into the calculations, so that a pure disintegration curve of the C'' product is obtained. The branching relationship, Ac-C'' : Ac-C is calculated from the ionising relationship of C'' : C, on the assumption that in the appropriate equations one pair of proportionality factors varies as the ionising action of the α-particles of Ac-C and Th-C, whilst the second pair varies as the absorption coefficients of the β rays of Ac-C'' and Th-C''. The relationships found are Ac-C'' : Ac-C' $=99{\cdot}84$ and Ra-C'' : Ra-$C=0{\cdot}0004$. J. F. S.

Nomenclature of the Radioactive Families. M. C. NEUBURGER (*Physikal. Zeitsch.*, 1921, **22**, 247—248).—The author proposes a modified nomenclature for the radioactive families; this includes the terms, principal family, root family, and branch family. The principal families are the uranium and thorium families, and include the whole of the products of disintegration of these elements respectively. The root family, and there is only one, is that portion of the uranium family before the branching into ionium and uranium-Y; it consists therefore of the series $U_1 \longrightarrow U\text{-}X_1 \longrightarrow U\text{-}X_2 \longrightarrow U_2$. There are two branch families, namely, ionium $\longrightarrow$ the final products, and uranium-Y $\longrightarrow$ the final products. J. F. S.

States of Iron in Nitric Acid. JOSEPH GRANT BROWN (*J. Physical Chem.*, 1921, **25**, 429—454).—The author has measured the *E.M.F.* of cells of the type Fe|HNO_3 soln.||HNO_3(conc.)|Pt, in which, the nitric acid varied between *d* 1·01 and 1·41 and the iron electrode was sometimes rotated and sometimes still during the measurement. The *E.M.F.* was measured repeatedly from the moment of immersion of the electrode until a steady state was obtained. The surface of the electrode in the motionless experiments was examined microscopically, The results are discussed at length and the author is of the opinion that active iron is ferrous, that is, it sends ferrous ions into the solution, whilst passive iron is ferric. J. F. S.

The Theory of the Pile. DÉCOMBE (*Compt. rend.*, 1921, **173**, 834—836).—The author proposes to base the theory of the hydroelectric pile on the proposition that the non-compensated heat developed in a pile in action by the chemical reaction proceeding in it is equal to the Joule heat, ri^2dt, which is developed therein by virtue of its internal resistance r and of the current i which is circulating. This is discussed from a theoretical point of view. W. G.

Potential of the Thallium Electrode and the Free Energy of Formation of Thallous Iodide. GRINNEL JONES and WALTER CECIL SCHUMB (*Proc. Amer. Acad. Arts Sci.*, 1921, **56**, 199—236).—Measurements have been made at 25° and 0° of the conductivity and ionisation of thallous nitrate solutions, of the solubility of thallous chloride and of thallous iodide, and of the normal potentials

of the thallium and the iodine electrodes. From the conductivity data the equivalent conductance of the thallium ion was found to be 78·36 mhos at 25° and 41·8 mhos at 0°. The equivalent concentrations of the ionised fractions of thallous chloride and thallous iodide, calculated from the conductivity of saturated solutions of these salts, are, respectively, 0·014094 and 0·000235 at 25°, and 0·006095 and 0·0000587 at 0°. From the potential measurements it has been computed that the normal potential of the thallium electrode is +0·6188 volt at 25° and +0·5885 volt at 0°, and that of the iodine electrode −0·3406 volt at 25° and −0·3399 volt at 0°. From the foregoing results, the following are computed for the reaction: Tl (solid) +0·5 I_2 (solid)=TlI (solid): free energy of formation (A)=125·79 kj. at 25° and 125·48 kj. at 0°; heat of formation (U)=122·11 kj. at 25°. Contrary to the assumptions of earlier investigators, it has been found that a metallic thallium electrode is more negative than a saturated two-phase amalgam electrode by 2·8 millivolts at 25° and 1·8 millivolts at 0°.

CHEMICAL ABSTRACTS.

Electrolysis of Hot Concentrated Sulphuric Acid. HANS HOFFMANN (*Zeitsch. Elektrochem.*, 1921, **27**, 442—445).—The author has electrolysed concentrated sulphuric acid (98·3%) d_4^{18} 1·841 at a series of high temperatures by currents of various strengths. It is shown that at 50°, independently of the current strength, hydrogen, hydrogen sulphide, and sulphur are produced on the cathode, whilst at higher temperatures sulphur dioxide and sulphur are produced and in the neighbourhood of 300° only sulphur is obtained. Oxygen is liberated from the anode at these temperatures. At 200°, the oxygen is mixed with sulphur dioxide, produced from sulphur which has diffused from the cathode chamber, and has been oxidised by the hot sulphuric acid and the nascent oxygen. From 280° upward sulphur dioxide and oxygen are liberated in quantities corresponding with Faraday's law. The gas element $SO_2|O_2$, in consequence of incomplete charging of the electrodes, does not furnish the expected *E.M.F.*, and also the velocity of reaction of the gases is too small for the production of large quantities of current. The technical possibilities of such a cell are regarded as hopeless. The decomposition voltage of hot concentrated sulphuric acid lies near to that of water, that is, higher than the calculated and observed values of the potential difference of the gas element. From this it follows that the primary products of electrolysis are hydrogen and oxygen whilst sulphur dioxide is a secondary product.

J. F. S.

Structure of Metal Electrolytically deposited on Rotating Cathodes. W. E. HUGHES (*J. Physical Chem.*, 1921, **25**, 495—509).—A discussion on the structure of metals which have been deposited electrolytically on rotating cathodes. It is suggested (1) that the polished appearance often observed on the surface of deposits formed on rotating cathodes is due to the smallness of the grains

composing the deposit, (2) that the smallness of grain is a consequence of the constancy of metal concentration at the cathode surface, and (3) that, since mechanical movement can maintain a constant metal concentration, rotation of the cathode operates in that way in the cases of deposits formed on rotating cathodes and not, as has been suggested, by way of burnishing. J. F. S.

Influence of Chlorides on the Decomposition Voltage Curve of Chromic Acid. E. LIEBREICH (*Zeitsch. Elektrochem.*, 1921, **27**, 452—455).—The thin layers of oxide or hydroxide on the cathode which give rise to the periodic phenomena observed during the electrolysis of chromic acid are shown to be colloidal in nature; the oxide is drawn to the cathode just so long as a negative tension lies on it. The addition of chlorides brings about a displacement of two curves which make up the decomposition voltage curve of chromic acid. J. F. S.

Calculation of the Specific Heat of Gases. II. W. HERZ (*Zeitsch. Elektrochem.*, 1921, **27**, 474—475; cf. this vol., ii, 299).—A theoretical paper in which the author has deduced four equations by means of which the difference between the two specific heats of gases may be calculated. The first of these, $C_p-C_v=\gamma/M^{1/3}d^{2/3}(T_k-T)$ in which γ is the surface tension is deduced from the Eötvös rule for non-associated liquids. According to Lorenz (A., 1916, ii, 240), the quotient of the density at the boiling point and the critical density is approximately equal to 2·66, whence the second equation, $C_p-C_v=0{\cdot}75d_s/d_kM$, is obtained. The third equation, $C_p-C_v=cL/MT_s^2$, in which c is the boiling-point elevation constant and L the latent heat of vaporisation, is obtained from van't Hoff's boiling-point relationship. The fourth equation is obtained by combining Eötvös's rule with Oswald and Davies's equation, $T_k=(1/K_{20}+293)/2$ (*Zeitsch. anorg. Chem.*, 1920, **112**, 278). This has the form $C_p-C_v=(1/K_{20}+273)/MT_k$, in which K_{20} is the coefficient of expansion at 20°. The values of C_p-C_v calculated by each of these equations is compared with the experimentally determined values of twelve substances of widely differing character; a fair agreement is found in all cases. In the first equation, the variations from the accepted value lie between +5·5% and −12%, in the second equation between +6% and −27%, in the third equation between +6% and −21%, and in the fourth equation between +2% and −18%. J. F. S.

Fielding's Formula connecting Critical Temperatures and Pressures. J. NEWTON FRIEND (*Chem. News*, 1921, **123**, 219—220).—The author shows that the formula recently put forward by Fielding (A., 1919, ii, 45) connecting critical temperature with critical pressure has a theoretical basis and may be evolved from the van der Waals equation. The formula has the form $T_c=K\sqrt{p_c}+x$, in which K and x are constants. The author shows that the expression $T_c=8/R\sqrt{\alpha p_c/27}$ is readily obtained. If now $\sqrt{\alpha}/R$ remains fairly constant, as is quite possible at least for allied elements, the equation may be written $T_c=K\sqrt{p_c}$, where K is a

constant equal to $8\sqrt{\alpha}/R\sqrt{27}$. This expression is the essential feature of Fielding's equation, and since it is not to be expected that $\sqrt{\alpha}/R$ is even approximately constant for all the elements, it is not surprising that Fielding finds notable exceptions to his formula. Hence there is not only a theoretical basis for the formula but also an explanation for the exceptions. J. F. S.

Latent Heat of Vaporisation. J. C. THOMPSON (*Chem. News*, 1921, **123**, 204—206).—On the bases of several unusual assumptions, the author deduces a formula for calculating the latent heat of vaporisation. The formula has the form $P\log_{10}P/10{\cdot}31\times D^{4\,3}=L$, in which P is the ratio between the density of a liquid and its vapour at the boiling point, and D is the density of the liquid at the boiling point compared with water at 4°. The assumptions made in the deduction of the formula are: (i) molecules do not collide, but pass sufficiently near to each other for the forces of attraction between them to be constantly altering the direction of movement. The forces of attraction probably consist of ordinary gravitational force together with surplus or unsaturated valency force, (ii) molecules are without size, (iii) a liquid is merely a gas under the pressure produced by the attractive force of its molecules, (iv) a solid is a liquid in which the attractive forces of the molecules are different in different directions, (v) a crystalline solid is a solid in which the major attractive forces are all acting in one direction, and the minor forces in another. The values calculated for the latent heat by means of the above formula agree remarkably well with the accepted experimental values; thus: water 536·6 (536·6), ethyl ether, 87·58 (87·4), benzene, 95·21 (96·1), and oxygen, 52·3 (52·0); the accepted values are given in brackets. J. F. S.

Specific Heat of Vapours. Determination of Specific Heat of a Vapour at Constant Pressure, *Cp*. J. C. THOMPSON (*Chem. News*, 1921, **123**, 220—221).—A theoretical paper in which a method of calculating the specific heat of gases at constant pressure is outlined, which, although not theoretically sound, yields fairly correct results. The axioms (i), (iii), (iv) in the preceding abstract and those following are discussed. (*a*) The size of molecules does not in any way influence the volume occupied by a liquid. (*b*) A crystalline solid is so arranged that equal forces always act in the same direction. The growth of a crystal from solution is explained on this hypothesis, as the molecules in separating from solution will attach themselves to the small crystal so that the greater forces act on the greater forces. J. F. S.

Necessity of bringing Concordance into the Thermochemical Data of Organic Compounds. WOJCIECH SWIENTOSLAWSKI (reprint from *Roczniki Chemji*, **1**, 59—103).—The author reviews a large number of thermochemical data of organic compounds and discusses the experimental basis of the results. He maintains that a single organic substance ought to be chosen as the standard of thermochemical data; this substance should be benzoic acid, the heat of combustion of which should be determined

with the greatest precision and the value obtained accepted as an international standard. The value ought to be expressed in calories and not in absolute units, since it is impossible to determine the latter quantity with the necessary precision. Calorimetric bombs should always be standardised by means of this substance, and authors of work in the thermochemistry of organic compounds should always state full details of the standardisation of the bomb so that recalculation of the results may be possible.

J. F. S.

Divergence between Adiabatic and Ordinary [Thermochemical] Measurements. W. SWIENTOSLAWSKI and HELENA I ZOFJA BŁASZKOWSKIE (*Roczniki Chemji*, **1**, 166—170).—The authors have carried out thermochemical measurements under differing conditions; (1) in an ordinary calorimeter in which the temperature of the outer jacket was kept constant; (2) in an ordinary calorimeter in which the evaporation of water was prevented by covering it with a layer of a very slightly volatile liquid; and (3) in an adiabatic calorimeter. The results obtained show that the figure obtained by the measurement of a constant quantity of heat in an ordinary calorimeter differs from the value obtained for the same quantity in an adiabatic calorimeter according to the conditions under which the measurement is made. The difference in the two values varies between $\pm 0.03\%$ and $\pm 0.46\%$. J. F. S.

Substantive Cotton Dyeing. RUDOLF AUERBACH (*Kolloid Zeitsch.*, 1921, **29**, 190—193).—The velocity of diffusion of a number of substantive cotton dyes into a 4% gelatin jelly has been determined at 20°. The distance to which the dye has diffused was measured after twenty-four, thirty-six, sixty, and eighty-four hours and comparative measurements were made with 0·1, 0·05, and 0·01% solutions of the highly-dispersed crystal-violet. It is shown that dyes which are adsorbed from cold solution, diffuse at an average rate of 3·5 mm. per day from 0·1% solutions, whereas dyes which are adsorbed from warm solutions under the same conditions diffuse at 0·9 mm. per day. Potassium dichromate will also dye cotton, but if the dyed material is washed with either water or alcohol the dichromate is all removed, but in washing with mixtures of alcohol and water it is found that less dichromate is removed as the alcohol concentration increases up to a maximum alcohol concentration of about 65%, after which more dichromate may be washed out. It is suggested that the dispersion of the dichromate is at its minimum in the presence of 65% alcohol.

J. F. S.

The Empirical Formula of Walden and the Theory of Ghosh. (MLLE) H. KADLCOVÁ (*Chem. Listy*, 1921, **15**, 109—110).—The values obtained for the empirical constant of Walden (A., 1920, ii, 598—600) $D\sqrt[3]{v}$ as determined by himself and those resulting from calculations according to Ghosh's theory (T., 1918, **113**, 449; 1920, **117**, 1390) for different degrees of dissociation, although in close agreement, are not identical. Since

a comparison of the results of both Walden and Ghosh leads to the conclusion that for a definite degree of dissociation the value of $D\sqrt[3]{v}$ is a constant, it may also be concluded that an electrostatic attraction really exists in solution between electrolytic ions having charges in agreement with the charge of ordinary electrons. The supposition of Ghosh that strong electrolytes are completely dissociated especially in concentrated solutions does not seem warranted. CHEMICAL ABSTRACTS.

Bragg's Work and the Law of Definite Proportions. A. QUARTAROLI (*Gazzetta*, 1921, **51**, ii, 211—212).—The author replies to Perucca's criticism (this vol., ii, 493) on his previous paper (A., 1920, ii, 602). T. H. P.

Possible Utilisation of the Diagrams of Diffraction of X-Rays for the Complete Determination of the Structure of Quartz. CH. MAUGUIN (*Compt. rend.*, 1921, **173**, 719—721).—A discussion of the results obtained by radiograms prepared according to Laue's method with a consideration of their use in calculating the value of the parameters used by Bragg in his definition of the structure of quartz. W. G.

X-Ray and Infra-red Investigations of the Molecular Structure of Liquid Crystals. J. STEPH. VAN DER LINGEN (*J. Franklin Inst.*, 1921, **192**, 511—514).—A thin pencil of X-rays has been passed through a thin layer of *p*-azoxyanisole and the pattern produced examined. In the case of the solid substance irregularly placed spots are observed which indicate that the crystalline layer is made up of small crystal units of about 1 mm. cross-section. On heating until the *p*-azoxyanisole is plastic and again examining the pattern, it is found that a point pattern is obtained which gives no indication of the type of the crystal symmetry. On heating further until the anisotropic liquid is obtained, a new type of pattern is observed consisting of a series of faint horizontal lines, which are about 1 mm. broad for those lines which pass through the central spot; further off they are fainter, thinner, and more closely spaced. If this is due to diffraction from parallel layers of lamellar molecules, the spacing between the molecules must be of the order 40 Å.U. The absorption spectra of solid, anisotropic liquid, and amorphous liquid forms of *p*-azoxyanisole and the ethyl ester of *p*-azoxycinnamic acid have been examined for infra-red light. It is shown that in all cases the spectra are alike, hence no change has taken place in the linking of the atoms in the molecule. If changes in the space lattices be due to changes in the molecules of polymorphous substances, then these changes are not due to changes in the radicles, but to a spatial rearrangement of the component parts of the molecules. J. F. S.

The Hydroxyl Ring. H. T. F. RHODES (*Chem. News*, 1921, **123**, 249—250).—A continuation of the author's previous work on the constitution of crystal hydrates (this vol., ii, 255). In the present paper, the constitution of the molecule of crystalline copper

sulphate is considered. The author considers that one molecule of water differs from the remaining four, because on treating the pentahydrate with ammonia, only four molecules of water are replaced by ammonia to form the tetra-amminomonohydrate of copper sulphate, whilst treating the penta-ammino derivative with water all five ammino-groups are replaced by water. It is shown that, with the exception of a few special cases, the hydrates of salts may be classed in four types of different constitution. J. F. S.

Is there Redissolution of Sodium Chloride in the Presence of a Non-congruent Solution submitted to Evaporation? C. RAVEAU (*Compt. rend.*, 1921, **173**, 772; cf. this vol., ii, 31, 386).—A further reply to Rengade (cf. this vol., ii, 93). W. G.

Ionic Synergism. I. Experiments with Congo-rubin. L. MICHAELIS and C. TIMÉNEZ-DIAZ (*Kolloid Zeitsch.*, 1921, **29**, 184—190).—It is shown that in all the work on the influence of ions on the condition of colloids the influence of the ions of the solvent has been disregarded. Experiments have been carried out on solutions of congo-rubin to ascertain the influence of a number of sodium and potassium salts in the presence of known concentrations of hydrogen ions. It is shown that each individual type of kation has an action of characteristic strength on the condition of a colloid, which may be experimentally determined for the hydrogen ion, but can only be determined for the sodium or potassium ion by extrapolation for an infinitely small hydrogen-ion concentration of the solvent. The hydrogen and sodium or potassium ions in mixtures do not influence the activity according to an additive law, but rather according to the law that all combinations of these ions have the same action for which $(\log h_0/h) . (\log i_0/i) =$ constant. In the equation h is the concentration of hydrogen ions and i that of the alkali ions. The significance of h_0 and i_0 is seen as follows: if the condition of the reversible colloid solution is represented by Z, then, for a mixture of hydrogen ions of concentration h and alkali ions of concentration i, $Z=f(h.i.)$. If to change the condition to z in a definite time, a mixture of hydrogen ions, h_z, and alkali ions, i_z, is necessary. Then $h_0 = \lim h_z$ when $i=0$, and $i_0 = \lim i_z$ when $h=0$. h_0 and i_0 are the asymptotes of the hyperbola represented by the equation $(\log h_0/h) . (\log i_0/i) = k$, and have the values $h_0 = 10^{-4.02}$ and $i_0 = 10^{-0.1}$. The sodium and potassium ions behave in mixtures as though they were of the same type. The combination of calcium and hydrogen ions appears to follow a similar law to that obtaining for the alkali ions. J. F. S.

Dielectric Constants of Colloidal Solutions. RUDOLF KELLER (*Kolloid Zeitsch.*, 1921, **29**, 193—196).—The dielectric constant of a number of colloidal solutions has been determined by Drude's method. It is shown that solutions of hydrated colloids such as gelatin and albumin in certain circumstances exhibit abnormally low dielectric constants, whilst colloidal gold solutions have still lower values. The colloidal solutions which occur in natural organisms and contain electrolytes show occasionally an exceed-

ingly high dielectric constant. The terms acidic and basic lose their classical meaning in non-dissociated and associated solutions, since only dissociated solutions can be acid or basic. Not only dyes, albumin, and amphoteric substances, but also potassium hydroxide and hydrochloric acid in the region of medium dielectric constant are somewhat associated, that is, colloidal; at most they are molecular dispersed and not ion dispersed. They obtain the sign of their charge, not from their internal chemical constitutive properties, but from their relative surface charge toward the dispersion medium. Potassium hydroxide in positively charged toluidine is to be regarded as electro-negative, whilst hydrochloric acid in benzaldehyde is positive. J. F. S.

Colloidal Condition of Sparingly Soluble and Slightly Soluble Substances in Water and other Solvents: Experimental Confirmation of Gibbs's Principle. I. TRAUBE and P. KLEIN (*Kolloid Zeitsch.*, 1921, **29**, 236—246).—An examination of solutions of sparingly soluble substances such as aqueous solutions of hydrocarbons, alkyl haloids, higher alcohols and aliphatic acids, *i*-amyl alcohol, *i*-butyric acid, aniline, *m*-cresol, lead and calcium sulphates, silver chloride, and silver oxalate, by means of the Tyndall cone and the ultra-microscope, shows that the whole of such substances are partly or entirely colloidally dissolved. It appears to be general that in the solution of easily-soluble substances such as sodium chloride in water the transition from the solid homogeneous phase to the solution takes place in such a way that submicrons exist for a short period in the saturated solution. The above is probably true for solvents other than water; thus a solution of water in benzene or carbon tetrachloride shows a colloidal phase. The very poor surface activity of hydrocarbons and alkyl haloids in stalagometric investigations is to be attributed to the coarse dispersion. The diameter of a larger submicron is of the order 10^{-5} cm., whilst that of an individual molecule is 10^{-8} cm., so that the surfaces stand in the ratio $10^{-10} : 10^{-16}$. Such substances in solutions as submicrons only show greater surface activity, despite the strong Gibbs's positivity, when they are converted into molecules or the densest emulsions. The first case is observed with bases such as atropine and acids such as nonoic acid, and the second with indifferent narcotics such as chloroform. If the Traube narcosis hypothesis is substituted for Gibbs's positivity, then all abnormalities can be explained. It is shown by means of the ultramicroscope that surface active substances accumulate, in accordance with Gibbs's principle, at the interface, oil–water, air–water, and lecithin–water. The fall of concentration increases with the size of the Gibbs's positivity. Gibbs's negative substances do not show this accumulation, for in some cases the concentration decreases in the region of the surface. Sparingly soluble benzene derivatives such as xylidine and cresol are very highly colloidal, a fact which explains the ease with which such substances are adsorbed by charcoal. Investigation of the cataphoresis of such substances shows that the colloidal

particles of aniline, toluidine, xylidine, octoic acid, and nonoic acid migrate to the anode, whilst quinoline migrates to the cathode. Preliminary experiments in the adsorption of poisons by the surface of cells of blood corpuscles, yeast-cells, and bacteria-cells have been made, from which conclusions on the cell-destroying action of these substances may be drawn. J. F. S.

Precipitation of Colloids by Non-electrolytes. PAUL KLEIN (*Kolloid Zeitsch.*, 1921, **29**, 247—250).—The results of experiments on the coagulation of colloids by non-electrolytes are described. It is shown that, in the absence of electrolytes, surface active non-conductors are able to coagulate negatively-charged colloids (suspensoids and emulsoids). In some unpublished work, Traube has shown that suspensions of charcoal and sulphur are coagulated by surface active non-electrolytes as soon as the water is saturated with these substances. The same action is now observed for sols of negatively-charged colloids such as arsenic sulphide, albumin, gold, silicic acid, and mercury sulphide. In these cases, coagulation only takes place when the surface active substance in the finest possible state of division in alcohol solution is added to the colloid. Electro-positively charged sols such as ferric hydroxide and aluminium hydroxide are not coagulated under the above-named conditions. The coagulation of albumin by narcotics is irreversible as long as any of the narcotic remains adsorbed in the albumin. This fact will probably furnish the reason for the harmful and sometimes fatal action of narcotics. Coagulation by sparingly soluble surface active non-conductors probably takes place in two phases. The first phase consists in a reduction of the degree of dispersion by mutual coagulation of two colloids, whilst the second consists in the adsorption of the larger particles on the surface of the separated drops of the non-conductor. This view demands that the primarily-formed colloid of the non-conductor should have a positive charge. J. F. S.

Quantitative Methods of Coagulation for Suspensoids. FRIEDRICH VINCENZ VON HAHN (*Kolloid Zeitsch.*, 1921, **29**, 226—236).—Since the stability of suspensoids is determined almost entirely by means of the coagulation by electrolytes, by one or other of the methods, (*a*) the drop process (Schulze), (*b*) the titration process (Linder and Picton), (*c*) the mixture process, and since different investigators using these methods obtain widely differing results, the author has investigated these and other methods in the case of arsenic sulphide sols. It is shown that the mixture process is the most convenient, but the Schulze precipitation method has the advantage that very little (5 c.c.) of the sol is required for a determination. The titration process is not suitable for quantitative work, because the rate of addition of the electrolyte has a marked influence on the result. The author recommends the use of potassium chloride as a normal electrolyte for such determinations. Since it is quite possible that the electrolyte coagulation method is not suitable in all cases, for example, in the case of very dilute

sols or in those cases where chemical combination occurs between the sol and the coagulating electrolyte, the author has tested other methods of coagulation, which include, (1) the effect of filtration on the sol, (2) effect of boiling, and (3) the effect of an electric current. Filtration influences a sol in the sense of causing an increase of the size of the particles. Particularly in the case of very dilute sols is it possible to obtain trustworthy data on the stability of the sol by making a partition curve of the sediment obtained from a series of successive filtrations. An approximate measure of the stability of a sol can be obtained by placing a drop of the sol on a filter-paper and measuring the ratio of the radius of the surface moistened by the unchanged sol to that of the surface moistened by the dispersion medium. This ratio, termed the "capillary number," is characteristic of the sol. The boiling test of stability is very easily carried out, but the method is not suitable for dilute sols, and is only to be regarded as a confirmatory test to the electrolyte coagulation method, or as a substitute for this in cases where chemical reaction occurs between the electrolyte and the sol. Experiments make it likely that coagulation by boiling depends on an adsorption process at the liquid vapour interface. The time required by a definite current to effect coagulation of a sol can be used as a measure of the stability. J. F. S.

Emulsions. III. Further Investigations on the Reversal of Type by Electrolytes. SHANTI SWARUPA BHATNAGAR (T., 1921, **119**, 1760—1769).

Graphical Representation of certain Heterogeneous Equilibria. A. C. D. RIVETT (*Chem. News*, 1921, **123**, 251—252).—A theoretical paper in which it is shown that the usual method of graphical representation of equilibria in binary and ternary heterogeneous systems often expresses relationships which are in opposition to the principles of the phase rule. A modified method of representation which avoids such anomalies is put forward.

J. F. S.

The Oxidation of Ferrous Salts by Potassium Ferricyanide. M. HANNIK (*Chem. Weekblad*, 1921, **18**, 615—616).—The experiments were made with solutions containing 0·007163 gram-molecule of reagent per litre, in presence of concentrated ammonium thiocyanate solutions; the equilibrium examined was therefore

$$Fe(CNS)_2+(CNS)'+Fe'''(CN)_6 \rightleftarrows Fe(CNS)_3+[Fe(CN)_6]''''.$$

The ferric thiocyanate formed or remaining in the solution (the equilibrium position was determined from both end-systems) was determined colorimetrically.

The oxidation of the ferrous salt was found to be almost quantitative, completely so in presence of excess of either reagent (ferrous salt or ferricyanide). The reverse reaction proceeds to a small extent only even in the presence of excess of ferrocyanide. In the

ordinary preparation of Turnbull's blue, the equilibrium is affected by the action of the ferrocyanide formed on the ferrous salt present.

S. I. L.

Landolt's Reaction. II. Some Reactions Analogous to the Landolt Reaction. J. EGGERT and B. SCHARNOW (*Zeitsch. Elektrochem.*, 1921, **27**, 455—470).—It was previously found in the kinetic investigation of the Landolt reaction, which takes place according to the equations, (1) $IO_3'+3SO_3''=I'+3SO_4''$, (2) $IO_3'+5I'+6H^{\cdot}=3H_2O+3I_2$, (3) $I_2+SO_3''+H_2O=SO_4''+2I'+2H^{\cdot}$, that the iodine-ion formation up to the liberation of free iodine takes place according to the equation $t=1/(k_2-k_1)\log_e(1+(k_2-k_1)x/k_1a)$, where k_1 and k_2 are the reaction constants of (1) and (2) respectively. The equation $T=1/(k_2-k_1)\,.\,\log_e k_2/k_1$ holds for the turning point where all the sulphite-ion has been used up, that is, where $x=a$. The time of the turning point is therefore independent of the concentration of the sulphite-ion, but inversely proportional to the concentration of the iodate-ion. The object of the present investigation is to find whether, by employing other reducing agents than sulphurous acid, the more general case exists, namely, that in which the third partial reaction is also determinative of the time of the turning point. For this purpose, the reducing agents potassium ferrocyanide, arsenious acid, sodium thiosulphate, and hydroxylamine hydrochloride have been examined. It is shown that, with respect of the Landolt reaction, reducing agents may be divided into two groups; to the first of these, thiosulphate and sulphite belong. In these cases, the third reaction takes place more rapidly than the second all through the process, that is, at the turning point the reducing agent is all used up. Ferrocyanide and arsenite constitute the second group, and in these cases the third reaction may proceed more slowly than the second, that is, at the turning point only a portion of the reducing agent has been used. Hydroxylamine is a particular case in which the second reaction proceeds more rapidly than the first, and in consequence the Landolt effect is not observed. In the case of the reducing agents in the second group, the equation $t=1/(k_2-k_1)\,.\,\log_e\{1+(k_2-k_1)x/k_1a\}$ again holds, with the difference that at the turning point x is no longer equal to a but $x=na$, where n is a fraction representing the ratio between the amount of reducing agent used to the original quantity added. The experiments with these reducing agents show that the time of the turning point is independent of the initial concentration of the reducing agent, but inversely proportional to the iodate-ion concentration. Despite the fact that the whole of the reducing agent has not been used at the turning point, the Landolt effect is exhibited. The theory of the reaction demands, (1) that n shall be constant, (2) that the constants k_1 and k_2 shall be proportional to the iodate-ion concentration, and (3) that the velocities at the turning point are proportional, (*a*) for constant iodate-ion concentration, to the ferrocyanide-ion concentration, and (*b*) for constant ferrocyanide-ion concentration, to the iodate-ion concentration. These demands are fulfilled in

the case of ferrocyanide-ion and arsenite-ion. Whilst the constants k_1 and k_2 are of the same order in the ferrocyanide reaction, the mean relationship k_2/k_1 is $8 \cdot 4 \times 10^{-3}$ in the arsenite reaction, that is, the second reaction is 8000 times as rapid as the first. In the reaction between the iodate-ion and the thiosulphate-ion, the main reaction products are the sulphate-ion and the tetrathionate-ion, which demands a new method of calculating k_1 and k_2 and furnishes a new confirmation of the theory. Along with the ions named, an undetermined oxidation product of the thiosulphate is produced which reacts slowly with iodine to form sulphate. In consequence of the small amount (1·2%) of this product, the mechanism of the reaction is only slightly influenced. In the reaction between the iodate-ion and the hydroxylamine-ion, iodine is separated on mixing the reagents, but the blue coloration of the starch only takes place when the velocity of reaction $2NH_3 \cdot OH^{\cdot} + 2I_2 = N_2O + H_2O + 6H^{\cdot} + 4I'$ has become great enough to raise the iodine concentration to 10^{-6} gram per litre, that is, to the smallest amount recognisable by starch solution. The delayed blue coloration does eventually appear even in this case, but for quite other reasons, so that this reaction cannot be included in either of the other groups. J. F. S.

Intra-molecular Energy during Combustion. W. T. DAVID (*Phil. Mag.*, 1921, [vi], **42**, 868—870; cf. A., 1920, ii, **82**, 731; this vol., ii, 85).—A continuation of previously published work. In the present paper, the pre-pressure period and the explosion period of coal gas explosions are considered. The pre-pressure period is the interval between the time at which the igniting spark passes and that when the pressure commences to rise. In this interval, a considerable amount of gentle ignition occurs, but there is no rise of pressure. In the cases considered, the number of molecules after explosion is about 3% less than before combustion, consequently the translational energy of the freshly-formed molecules during this period is not greater than that of the molecules before ignition. There is no appreciable radiation emitted in this period. In the early stage of the explosion period, the pressure rises slowly, indicating that combustion is proceeding slowly and a small but appreciable radiation is emitted. The radiation of longer wave-length up to about 11 μ is emitted first, and then is accompanied by radiation of shorter wave-length. This is attributed to a moderated combustion being succeeded by a more vigorous combustion. In the later stages of the combustion period, combustion proceeds more violently, as is evidenced by a rapid rise in pressure, and in this period the ratio of infra-red radiation transmitted through quartz (up to 3·5 μ) to that transmitted through fluorite (up to 11·0 μ) is 0·55 for a 15% coal-gas mixture, 0·52 for a $12\frac{1}{2}$% mixture, and 0·46 for a 10% mixture. These results show that the more vigorous the combustion the greater the proportion of short infra-red radiation emitted and therefore the greater the proportion of energy acquired during this period by the vibratory degrees of freedom corresponding with the short

wave-length radiation relatively to that acquired by those degrees corresponding with radiation of greater wave-length.

J. F. S.

The Limiting Pressure of Autoxidation. W. P. JORISSEN (*Rec. trav. chim.*, 1921, **40**, 539—541; cf. A., 1919, ii, 62; this vol., ii, 99).—A critical review of the conclusions drawn by Weiser and Garrison (this vol., ii, 248) in which it is pointed out that as Centnerszwer (A., 1913, ii, 1052) has shown that phosphorus volatilises into pure oxygen at ordinary pressures, the explanation of the limiting pressure put forward by these investigators is not valid. An alternative interpretation of their seventh experiment is given, which is consistent with the author's conception of limiting pressure.

H. J. E.

The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Solutions containing Sucrose. GEORGE JOSEPH BURROWS (T., 1921, **119**, 1798—1802).

Catalysis [of the Decomposition] of Hydrogen Peroxide by Colloidal Manganese Dioxide. A. LOTTERMOSER and R. LEHMANN (*Kolloid Zeitsch.*, 1921, **29**, 250—260).—The velocity of decomposition of hydrogen peroxide by colloidal manganese dioxide in the presence of a number of neutral salts and bases has been examined at 30°. The manganese dioxide was prepared in the hydrogen peroxide solution by the action of an alkali hydroxide on potassium permanganate. It is shown that the reaction is very sensitive to accidental impurities, and also that the velocity depends on the order in which the reagents are added to the water in which the reaction takes place. In the present experiments, the reagents were added in the order: hydrogen peroxide, potassium permanganate, alkali. The electrolyte the influence of which is being studied was always added to the water before the reacting substances. The assumption that the increase in the velocity constants is to be explained by the formation and subsequent decomposition of a hydrogen peroxide salt could not be confirmed. The influence of the kations of the added salts, which all have the same anion, follows the lyotrope series $Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Ca^{\cdot\cdot} > Na^{\cdot} > K^{\cdot} > Li^{\cdot}$, in which $Ba^{\cdot\cdot}$ accelerates the reaction to the greatest extent and $Li^{\cdot}$ retards it the most. At higher concentrations, barium falls after calcium. $Mg^{\cdot\cdot}$ and $NH_4^{\cdot}$, on account of the reduction of the hydroxyl ion which they produce, strongly retard the reaction.

J. F. S.

Catalytic Hydrogenation of Organic Compounds by Base Metals at the Atmospheric Temperature. V. Influence of the Nature and Position of the Halogens in Organic Haloid Compounds on the Removal of Halogen by Catalytic Hydrogenation. C. KELBER (*Ber.*, 1921, **54**, [*B*], 2255—2260).—The rate of absorption of hydrogen by a solution of a gram-millimol of the substance in an excess of aqueous potassium hydroxide

solution in the presence of 3 grams of nickel catalyst has been examined in the cases of chloro-, bromo-, or iodo-acetic acids, phenylchloroacetic, phenylbromoacetic, α-bromopropionic, *o*-, *m*-, and *p*-chloro-, bromo-, and iodo-benzoic acids, *o*-, *m*-, and *p*-chlorophenol, *o*- and *p*-bromophenol, *p*-iodophenol, and the chlorocresols. The rate of removal of the halogen by catalysis increases with increasing atomic weight of the halogen, and is in general more readily effected with aromatic than with aliphatic compounds. The distinction between the two classes of compound is less obvious with increasing atomic weight of the halogen. In aromatic compounds in which a second substituent is present, the halogen atom in the ortho-position is least readily and that in the para-position most easily replaced by hydrogen. H. W.

Formation of Elements and Structure of the Atomic Nucleus. EMIL KOHLWEILER (*Physikal. Zeitsch.*, 1921, **22**, 243—246).—A theoretical paper in which, on the basis of the hypothesis previously put forward by the author (A., 1920, ii, 610, 615, 744), and certain emendations necessitated by the recent work of Aston and Rutherford, the author draws up tables of the possible isotopes of many of the elements up to chromium. The atomic mass of the various elements is calculated and found generally to agree well with the accepted experimental values. J. F. S.

The Structure of the Static Atom. IRVING LANGMUIR (*Science*, 1921, **53**, 290—293).—Mathematical. Stability is obtained by the assumption of a repulsive force $Fq=(nh/2\pi)^2\{[(1/m)+(1/M)]/r^3\}$ between an electron of charge e and mass m, and a nucleus of charge Ze and mass M, where n is an integer denoting the quantum state of the electron. The important consequences of Bohr's theory all follow from this one also, and the present theory is much simpler when applied to polyelectronic arrangements.

CHEMICAL ABSTRACTS.

The Structure of the Helium Atom. IRVING LANGMUIR (*Physical Rev.*, 1921, **17**, 339—353; cf. A., 1920, ii, 656).—Besides the semi-circular model of the helium atom developed in the paper referred to, the author here develops a double circle model in which the two electrons move in two separate, parallel, circular orbits. This model, however, is unstable, and the ionising potential, computed by applying the quantum theory, is negative. Moreover, the magnetic moment is not zero. The behaviour of the semi-circular model is analysed in greater detail than in the preceding paper. In the case of coupled electrons the quantum theory should be applied, not to the momentum of the individual electrons according to the relation $\int pdq=h/2\pi$, but rather to the momentum which, by being relayed from one electron to another, passes in each direction around the nucleus. CHEMICAL ABSTRACTS.

The Dimensions of Atoms and Molecules. W. L. BRAGG and H. BELL (*Nature*, 1921, **107**, 107).—When estimates are made

from crystal data and from viscosity data of the diameters of the outer electron shell of the inert gases, the results do not show numerical agreement, but the difference between the two estimates is almost constant; that is, the increase in the size of the atom as each successive electron shell is added is nearly the same (except in the case of neon), whether measured by viscosity or by crystal data. It is indicated that (*a*) the elements at the end of any one period in the periodic table are very nearly identical as regards the diameters of their outer electron shells, and (*b*) in passing from one period to the next there is a definite increase in the dimensions of the outer electron shell. Measurements of the infra-red absorption spectra of hydrogen fluoride, hydrogen chloride, and hydrogen bromide lead to the same conclusions. It appears that the forces binding the atoms together are localised at that part of the electron shell where linking takes place. A. A. E.

Molecular Structure and Energy. J. R. PARTINGTON (*Nature*, 1921, **107**, 172).—The models postulated by Lewis and Langmuir, and supported by Rankine's viscosity data, for the molecules of certain halogens, nitrogen, nitrous oxide, nitric oxide, and carbon dioxide, are not in agreement with the specific heats of these gases. A. A. E.

Molecular Structure and Energy. A. O. RANKINE (*Nature*, 1921, **107**, 203; cf. preceding abstract).—A criticism of Partington's views on the apparent discrepancy between Lewis's and Langmuir's models and specific heat measurements. Even if the necessity for revising earlier ideas of energy partition on the basis of the quantum theory is entirely left out of account, it is pointed out that the nitrogen molecule is not spherically symmetrical in the same sense as are the atoms of the inert gases, there being two separate massive nuclei instead of one. Further, it is suggested that the nuclei of all polyatomic molecules may be capable of vibration to and fro. A. A. E.

Isotopes: their Number and Classification. WILLIAM D. HARKINS (*Nature*, 1921, **107**, 202—203; cf. this vol., ii, 445, 582).—The author's theory of nuclear building is supported by the observation that elements of even atomic number consist of more than twice as many isotopes as elements of odd atomic number. In nearly all atoms the number of positive electrons and the number of negative electrons are even, whilst the atomic number is even in 89% of the atoms in the surface of the earth and in 98% of those in meteorites. Most atom nuclei have the formula $(p_2e)_M$, where M is an even number. It is proposed to classify atoms according to their isotopic number, n, which when added to twice the atomic number gives the atomic weight. The value n may be defined as the number of neutrons (pe) which would have to be added to the atom of the same atomic number, but of zero isotopic number, to give the composition of the nucleus. Thus the formula of any nucleus would be $(p_2e)_M(pe)_n$. The isotopic numbers of

elements of even atomic number are mostly even, whilst those of odd atomic number are mostly odd. Graphs showing the relation between the isotopic numbers of elements and their abundance in the earth's crust or in meteorites exhibit well-defined, almost identical, maxima and minima. A. A. E.

Alteration of the Basis of the Atomic Weights and Decennial Revision of the Atomic Weight Table. G. ODDO (*Gazzetta*, 1921, **51**, ii, 161—168).—The history of the controversy concerning the use of the H=1 or the O=16 basis for the calculation of the atomic weights of the elements is outlined, and it is pointed out that the values for the ratio O : H obtained by Stas (15·84—15·88), Keiser (1887), Cooke and Richards, Rayleigh (1889 and 1892), Noyes (1889), Dittmar and Henderson, Morley, Leduc, Thomsen, Berthelot, Keiser (1898), Rayleigh (1904), Guye and Mallet and Noyes (1908) lie between the limits 15·87 and 15·89. Since the value of this ratio is so accurately known, the author suggests that the use of atomic weights referred to the basis O=16 be abandoned. Arguments are also advanced against frequent revision of the atomic weights and the plea made that such revision be effected at ten-year intervals from the present year.
T. H. P.

The New International Commission on Chemical Elements. BOHUSLAV BRAUNER (*Chem. News*, 1921, **123**, 230—232).—The author recommends to the New International Commission that the term " atomic masses " be used only for the whole numbers of the isotopes *B* as determined by the physical (Aston's) method, and that the term " atomic weights " be applied to the numbers obtained by chemical methods, no distinction being made between pure elements, mixtures of isotopes, or single isotopes. He also proposes to call the sub-committee of the " International Commission on Chemical Elements " a " Sub-Committe for Atomic Weights."
W. P. S.

Valency and Co-ordination. SAMUEL HENRY CLIFFORD BRIGGS (T., 1921, **119**, 1876—1879).

Lecture Experiments on the Kinetics of Reactions in Solutions (Applied to the Landolt Reaction). J. EGGERT and B. SCHARNOW (*Ber.*, 1921, **54**, [*B*], 2521—2525).—The authors describe a series of eleven experiments on the reaction expressed by Landolt as the equations : $IO_3'+3SO_3''=I'+3SO_4''$, $IO_3'+5I'+6H^{\bullet}=3I_2+3H_2O$ and $3I_2+3SO_3''+3H_2O=6I'+6H^{\bullet}+3SO_4''$. The results obtained demonstrate the characteristic properties of the kinetics of coupled reactions with reference to the influence of the concentration of the components and to the action of catalysts.
T. H. P.

Inorganic Chemistry.

Preparation of Hydrogen by the Partial Liquefaction of Water-gas. GEORGES CLAUDE (*Compt. rend.*, 1921, **173**, 653—655).—Previous experiments for the preparation from water-gas of hydrogen for use in the synthesis of ammonia had to be abandoned in 1908 owing to difficulties (cf. *ibid.*, 1921, **172**, 974) that have now been overcome by certain simple devices. The water-gas from which a portion of the carbon monoxide has been removed by preliminary cooling is allowed to expand whilst doing external work and lubrication difficulties due to the low temperatures are overcome by the addition of 5% of nitrogen. In this way, it is easily possible, working on a large scale, to obtain a steady supply of hydrogen containing only 1·5% of carbon monoxide. [Cf. *J. Soc. Chem. Ind.*, 1921, 810.] W. G.

Negative Hydrogen Ions. ALFONS KLEMENC (*Zeitsch. Elektrochem.*, 1921, **27**, 470—474).—A theoretical paper in which the difference of energy between the hydrogen atom (H) and that of the negative hydrogen ion (H′) is deduced on the basis of Bohr's atomic model and the assumption that both electrons are in the same orbit. The relationship $H'=H+e+1/n^2.39{\cdot}4$ Cal. is obtained, from which it follows that the process is endothermic in respect of the electron affinity of the halogen atoms. The theoretical value is then calculated, by making use of the thermochemical data of lithium hydride, the specific heats and energy of dissociation of molecular hydrogen, the energy of ionisation of lithium, and Born's lattice energy. The quantity $H'=H+e+13\pm2{\cdot}8$ Cal. is obtained, but for perfect agreement the value $n=2$ must be introduced into the above equation. In view of this, it is stated (with reserve) that both electrons of the hydrogen atoms in lithium hydride must occupy the second Bohr orbit. It is possible that the negative hydrogen ion is formed during the determination of the heat of dissociation of hydrogen by Langmuir's method, but the velocity of the reaction appears to be too small for the energy change, 39·4 Cal. Several equilibrium constants connecting H_2, H, $H^{\cdot}$, and H′ are deduced on the basis of the Nernst equation.

J. F. S.

Magnetochemical Examination of Constitutions in Mineral Chemistry. I. The Sulphur Acids. PAUL PASCAL (*Compt. rend.*, 1921, **173**, 712—714).—The author has determined the molecular magnetic susceptibilities of the inorganic oxygenated sulphur compounds, the hydroxylaminesulphonates, the amidosulphonates, and the organic sulphinic and sulphonic acids, the sulphoxides and sulphones, and from his results has calculated the susceptibilities of the various radicles such as SO_4, SO_3, etc. The results furnish further proof of the constitution of sulphuric and

thiosulphuric acids, of the various thionic acids, and indicate that the sulphurous and sulphinic acids must contain the group SO:.
W. G.

Stability of Persulphates. K. ELBS and P. NEHER (*Chem. Zeit.*, 1921, **45**, 1113—1114).—Sodium, potassium, and ammonium persulphates can be preserved almost unchanged for years if kept dry and protected from sunlight. At ordinary temperatures, aqueous solutions show appreciable decomposition after some days, and with increasing temperature the rate of decomposition rapidly increases and is further accelerated by sunlight. At 100°, decomposition is practically complete in one hour, although the actual velocity varies to a considerable extent with the concentration of the solution, and with the nature of the kation, the sodium salt being somewhat more stable than the potassium and ammonium salts. The addition of sodium sulphate distinctly diminishes the velocity of decomposition, whilst the presence of 5% of sulphuric acid accelerates decomposition five to ten times. As an oxidising agent, sodium persulphate is the most useful salt, and it is often advantageous to diminish the velocity of the reaction, and so prevent loss of available oxygen evolved as gas, by adding about 20% of sodium sulphate (anhydrous) to the solution.
G. F. M.

Effect of Freezing on Colloidal Selenium. A. GUTBIER and F. FLURY [with FR. HEINRICH] (*Kolloid Zeitsch.*, 1921, **29**, 161—172).—A number of experiments on the influence of freezing on selenium sols are described. In the case of sols produced by the action of sulphur dioxide on solutions of selenious acid at 60°, it is shown that the destruction produced by freezing is greater the more completely the solutions have been purified by dialysis. The assertion of Lottermoser, that the factor which influences the precipitation of the colloid is not the amount of the reduction of temperature, but the complete solidification of the solution to an ice-like mass, could not be confirmed (A., 1909, ii, 27), for in the present experiments the solutions were completely frozen, but on melting the greater part of the colloid went back into solution. Sols produced as above, but at ordinary temperatures after freezing, yield on melting the typical selenium sols if they have not been kept frozen too long. If the freezing is repeated many times, or if the sol is kept in the frozen condition too long, the colour by transmitted light becomes less intense and the stability of the sol becomes much less, particularly toward an increase in temperature. It is also shown that the nature of the reducing agent employed in the preparation of the sols and the temperature of preparation have a great influence on the stability toward freezing. Sols prepared by reduction with hydrazine at 60° and dialysed are much more sensitive to freezing than similar sols prepared by reduction with sulphur dioxide at ordinary temperatures. The hydrazine sols coagulated irreversibly on cooling even before solidification occurred and a red deposit was formed on the bottom and top of the frozen mass. In the case of the sulphur dioxide

sols, it is shown that the concentration of the undialysed sol has a marked influence on the stability towards a reduction of temperature. The more concentrated sols are more readily destroyed by freezing than the more dilute solutions, and even in these cases it is found that on keeping the sol in the frozen state for some time an inhomogeneity is produced, and a red ring of precipitated selenium is formed at the top and bottom of the frozen mass.

J. F. S.

Viscosity and Molecular Dimensions of Gaseous Ammonia, Phosphine, and Arsine. A. O. RANKINE and C. J. SMITH (*Phil. Mag.*, 1921, [vi], **42**, 601—614).—The viscosity of ammonia, phosphine, and arsine has been determined by the method previously described (A., 1910, ii, 829) at various temperatures; similarly, measurements have been made with air for comparative purposes. The following values of the viscosity in C.G.S. units $\times 10^{-4}$ and Sutherland's constant, C, are recorded: air, $\eta_0=1{\cdot}724$, $\eta_{15}=1{\cdot}799$, $\eta_{100}=2{\cdot}191$ and $C=117$; ammonia, $\eta_0=(0{\cdot}943)$, $\eta_{100}=1{\cdot}303$, $C=(370)$; phosphine, $\eta_0=1{\cdot}070$, $\eta_{15}=1{\cdot}129$, $\eta_{100}=1{\cdot}450$, $C=290$; arsine, $\eta_0=1{\cdot}470$, $\eta_{15}=1{\cdot}552$, $\eta_{100}=1{\cdot}997$, $C=300$. The bracketed values are calculated from the mean of earlier observations of several investigators. By means of Chapman's formula, the area presented by the molecules for mutual collision has been calculated; this is $A=4\pi\sigma^2$ where σ is the radius of the molecule when treated as an attracting elastic sphere. The collision areas in cm.$^2\times 10^{-15}$ are found to be: ammonia, 0·640, phosphine, 0·911, and arsine, 0·985. The values previously given for the gases neon, argon, krypton, and xenon (*loc. cit.*) have been corrected for an error which was associated with the earlier work, and the following corrected values are given: neon, $C=69$, $\bar{A}=\pi\sigma=0{\cdot}417$, $\sigma=2{\cdot}30$; argon, $C=162$, $\bar{A}=0{\cdot}648$, $\sigma=2{\cdot}87$; krypton, $C=212$, $\bar{A}=0{\cdot}757$, $\sigma=3{\cdot}10$, and xenon, $C=283$, $\bar{A}=0{\cdot}915$, and $\sigma=3{\cdot}41$. J. F. S.

The Electronic Synthesis of Chemical Compounds. I. Formation of Ammonia. EGON HIEDEMANN (*Chem. Zeit.*, 1921, **45**, 1073).—By passing a mixture of pure hydrogen and nitrogen through an electron tube, maintaining a tension a few volts above the ionisation tension of both gases, a relatively high yield of ammonia was obtained. A parallel is drawn between photochemistry and electron chemistry, in which light and electrons are the respective activating agents. E. H. R.

Reaction of Nitrous Acid with Hydrazine and with Azoimide. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, **51**, ii, 201—207; cf. this vol., ii, 346).—The method given for the estimation of nitrous acid by Dey and Sen-Gupta (A., 1911, ii, 822; 1912, ii, 296), who find that a nitrite loses two-thirds of its nitrogen in the elementary state when treated with hydrazine sulphate, is not exact, since the decomposition of hydrazine nitrite in this way is accompanied by secondary reactions varying markedly with variation in the experimental conditions. Highly discordant results have, indeed,

been obtained by different authors who have investigated the decomposition of hydrazine nitrite (Girard and Saporta, A., 1904, ii, 678; Francke, A., 1906, ii, 82; Angeli, A., 1894, ii, 93; Curtius, A., 1893, ii, 372; Dennstedt and Göhlich, A., 1898, ii, 425; Sommer, A., 1913, ii, 952; Sommer and Pincas, A., 1916, ii, 316), and many different interpretations of the reaction have been advanced.

The author's experiments on the interaction of equivalent solutions of potassium nitrite and hydrazine sulphate in an atmosphere of carbon dioxide give the same result at the ordinary temperature as at the boiling point of the solution, the mixed gases evolved consisting of about 10·2—11·7% by vol. of nitrogen and 88·3—89·8% of nitrous oxide; this result is not in agreement with Girard and Saporta's equation (*loc. cit.*). When the proportion of nitrous acid taken is increased, the percentage of nitrogen present in the gases evolved at the boiling point of the liquid increases and, when $N_2H_4 : HNO_2 = 2 : 3$, $1 : 2$, and $2 : 5$, amounts to 41·8, 48·6, and 49·1 respectively. As regards the decomposition in presence of sulphuric acid, a solution containing 0·334, 0·334, and 0·334 gram-mol. per litre of hydrazine, nitrous acid, and sulphuric acid yields a mixture of 80% by volume of nitrous oxide and 20% of nitrogen, whilst with 0·334, 0·668, and 0·334 gram-mol., the percentages of the two gases are 68·1 and 30·9 respectively. These results show that the reaction between hydrazine and a nitrite cannot be used for estimating the latter, the nature of the gases liberated as well as their proportions varying with the conditions.

The author has also studied the action of hydrazine hydrate on free nitrous acid under diverse conditions, but in no case was it found possible to detect the formation of hyponitrous acid.

To the two principal reactions given by Sommer and Pincas (*loc. cit.*), it seems probable that there should be added that expressed by the equation $N_2H_4 + 2HNO_2 = N_2 + N_2O + 3H_2O$.

T. H. P.

Oxidation and Luminescence of Phosphorus. III. Catalytic Action of Vapours. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1921, **25**, 473—490; cf. this vol., ii, 248, 637).—The vapours of a number of organic compounds influence the rate of oxidation of phosphorus. Most of the vapours examined retard the oxidation, but nitrobenzene and diphenylamine accelerate it. Phosphorous oxide is an intermediate product in the oxidation of phosphorus to phosphoric oxide. The rapid oxidation of phosphorus to phosphorous oxide occurs at 27° in pure oxygen under 1 atm. pressure, whilst that of phosphorous oxide to phosphoric oxide under the same conditions occurs at 65°. As a rule, the heat of reaction of the first step raises the temperature in the reaction zone to the point where the lower oxide oxidises with sufficient velocity to emit light. In a stream of oxygen at temperatures below 27°, the small amount of phosphorus which vaporises is oxidised to phosphorous oxide, and this is slowly converted into phosphoric oxide without the emission of

light. In a stream of gas or vapour containing oxygen, the chief oxidation product is phosphorous oxide if the temperature is low, if the concentration of oxygen in the reaction zone is low, or if the vapours condense on the surface of the phosphorous oxide particles. The ions formed during the oxidation of phosphorus consist of oxide particles about charged nuclei and vapours are adsorbed or condensed both on the charged and uncharged particles. Condensed vapours decrease the conductivity of "phosphorised" air by weighting down the charged particles. If the adsorbed vapours react with phosphorous oxide they increase the velocity of oxidation of phosphorus both by removing oxide particles from the zone of reaction and by raising the temperature. Nitrobenzene and diphenylamine act in this way. If the adsorbed vapours are inert they prevent further oxidation of phosphorous oxide and also form a cloud near the surface of the phosphorus which retards the action. If two vapours are adsorbed to the same extent, the heavier one will form the denser cloud and will have the greater inhibiting action. It is concluded that vapours (with the exception of a trace of water vapour) which influence the rate of oxidation of phosphorus are not catalysts in the ordinary sense of the word. The vapours are merely condensed on the charged or uncharged products, and act as described above. The cloud surrounding the phosphorus approaches nearer the surface as the oxidation becomes less energetic, and may form a protecting film which reduces vaporisation and oxidation of the phosphorus to a minimum.

J. F. S.

Fusion of Carbon. Eugen Ryschkewitsch (*Zeitsch. Elektrochem.*, 1921, **27**, 445—452; cf. this vol., ii, 258, 586).—A description of further experiments on the fusion of carbon. It is shown that carbon can be melted under ordinary pressure by an electric current. The carbon always melts at the point where the current and consequently the temperature is the highest. Under suitable conditions, high current efficiency, and good heat insulation, carbon may be melted by comparatively small currents. The solidified drops of carbon and the two points from which the drop has fallen consist of pure graphite. The sublimation point of carbon at ordinary pressures lies very near to the melting point, and in consequence the failures to melt carbon described in the literature are to be attributed to the superposition of the sublimation over the melting. In saturated carbon vapour, unusually large and well-formed graphite crystals are produced, which grow in the planes of stronger affinity. The completely closed furnaces used in the melting of carbon have made a determination of the melting point impossible up to the present. J. F. S.

Viscosities and Molecular Dimensions of Methane, Hydrogen Sulphide, and Cyanogen. A. O. Rankine and C. J. Smith (*Phil. Mag.*, 1921, [vi], **42**, 615—620; cf. this vol., ii, 694).—The viscosities of methane, hydrogen sulphide, and cyanogen have been measured at 17° and 100°, and from the results the values of the Sutherland constant (C) and the collision area in $cm^2 \times 10^{-15}$

($\bar{A}$) have been calculated. The following values are recorded: methane, $\eta_0=1{\cdot}035$, $\eta_{17}=1{\cdot}094$, $\eta_{100}=1{\cdot}363$, $C=198$, and $\bar{A}={\cdot}0772$; hydrogen sulphide, $\eta_0=1{\cdot}175$, $\eta_{17}=1{\cdot}251$, $\eta_{100}=1{\cdot}610$, $C=331$, and $\bar{A}=0{\cdot}773$; cyanogen, $\eta_0=0{\cdot}935$, $\eta_{17}=0{\cdot}995$, $\eta_{100}=1{\cdot}281$, $C=330$, and $\bar{A}=1{\cdot}21$. The viscosity values are given in C.G.S. units $\times 10^{-4}$.

J. F. S.

Helium-bearing Natural Gas. G. Sherburne Rogers (*U.S. Geol. Survey, Prof. Paper*, 1921, No. 121, 113 pp.).—A résumé of the chemistry of helium and the radioactive elements, and a detailed account of the distribution, chemical composition, and chief sources of helium-bearing natural gas. Helium constitutes from 0·5 to 2% of certain nitrogen-rich natural gases occurring in Kansas, whilst natural gas occurring in Europe contains a maximum of only 0·38% helium. [See *J. Soc. Chem. Ind.*, 1921, Dec.]

J. S. G. T.

Some Properties of Fused Sodium Hydroxide. Thomas Wallace and Alexander Fleck (T., 1921, **119**, 1839—1860).

Conversion of Ammonium Sulphide and of Thiosulphates into Sulphates. W. Gluud (*Ber.*, 1921, **54**, [*B*], 2425—2426).—At 100°, ammonium sulphide in aqueous solution may be readily and completely converted into ammonium sulphate by air under a pressure of 10 atmospheres. Under similar conditions, sodium thiosulphate undergoes total transformation into sulphate, provided that sufficient alkali is present to unite with the sulphuric acid formed from the sulphur; if such excess of alkali is lacking, part of the sulphur separates in the elementary condition. A lower pressure than that mentioned above may be used, but in such case either the temperature must be raised or the duration of the action increased.

T. H. P.

The Melting and Boiling Points of Ammonium Sulphate. Ernst Jänecke (*Zeitsch. angew. Chem.*, 1921, **34**, 542—543; cf. A., 1920, ii, 757).—The equilibrium between ammonia, ammonium sulphate, ammonium hydrogen sulphate, sulphuric acid, and water has been further investigated and the results are shown graphically. Ammonium sulphate when heated evolves more ammonia than water, so that a certain amount of ammonium hydrogen sulphate (m. p. 147°) is first formed, and later this loses water, giving the pyrosulphate. The equilibrium diagram is also augmented by the inclusion of an acid sulphate, $NH_4{\cdot}H_3(SO_4)_2$ (m. p. 48°), and an ammonia compound $(NH_4)_2SO_4,2NH_3$. There are eutectics between sulphuric acid and the acid sulphate (m. p. −20°), between the acid sulphate and the hydrogen sulphate (m. p. 39°), and between the latter and the pyrosulphate (m. p. 138°).

A. R. P.

The Graphitic Nature of the Carbon of Nitro-lime. Naoto Kameyama (*J. Chem. Ind. Japan*, 1921, **24**, 1131—1142).—It is found that the carbon which separates when nitro-lime is treated with concentrated hydrochloric acid and 55% hydrofluoric acid is

entirely graphitic. This was proved by the specific gravity (2·246), the heat of combustion (7,857 cal. per gram), the diffraction rings formed by *X*-rays, the electrical conductivity and by oxidation to graphitic acid, satisfactory coincidence being obtained in parallel experiments with Acheson graphite. K. K.

The Octahydrate of Magnesium Sulphate. SHIRÔ TAKEGAMI (*J. Chem. Soc. Japan*, 1921, **42**, 441—453; cf. this vol., ii, 30).—The equilibrium systems of magnesium sulphate, sodium sulphate, and water at 25° and 30° were studied, and the existence of the octahydrate of magnesium sulphate was proved. (From these results it is deduced that in the equilibria of the reciprocal salt pairs, sodium chloride and magnesium sulphate and sodium sulphate and magnesium chloride at 25° there are ten solid phases, not nine as previously stated (*loc. cit.*), the phase $MgSO_4,8H_2O$ having to be added although its numerical values are still lacking.) The solid phase (der Bodenkörper) of the system at 25° is always the octahydrate. At 30°, also when the solution contains less than 32% of sodium sulphate, the solid phase is the octahydrate, which, however, is replaced by the heptahydrate when the concentration of the sodium sulphate exceeds 32%. When the solution contains about 7—9% of sodium sulphate, the solid phase below 45·5° is the octahydrate, whilst between 46·1° and 77·2° it is the heptahydrate. From the transition point in the presence of sodium sulphate, the following points are deduced for the case of magnesium sulphate alone:

$$\text{Octahydrate} \underset{\longleftarrow}{\xrightarrow{48\cdot2^\circ}} \text{heptahydrate} \underset{\longleftarrow}{\xrightarrow{\text{above } 77\cdot2}} \text{hexahydrate.}$$ K. K.

The Atomic Volume of Isotopes. FREDERICK SODDY (*Nature*, 1921, **107**, 41—42).—Values obtained for the density and atomic weight of ordinary lead, lead from thorite, and lead from uranium minerals have been compared. It is concluded that the atomic volumes cannot differ by so much as three parts in ten thousand and the atomic diameters by so much as one part in ten thousand. A. A. E.

The Purification of Mercury. C. HARRIES [and FRITZ EVERS] (*Zeitsch. angew. Chem.*, 1921, **34**, 541—542).—In order to test the value of the method described previously (this vol., ii, 552) for the purification of mercury, comparative tests on a 1% lead amalgam were carried out. One portion was allowed to fall twice through a long column of nitric acid (*d* 1·175); the resulting product contained no trace of lead, but the loss of mercury was 3·7%. A second portion was heated for ten hours at 150—160° while passing a current of air through it; the resultant metal was left for several hours in contact with strong hydrochloric acid, and, after thorough washing with water, was found to be free from lead. The loss of mercury in the latter case was only 2%. An amalgam containing 1% of tin after three passages through nitric acid lost 9·2% of its mercury content and the remaining metal still contained traces of tin. Treated by the hot air method, it

lost only 1·4% of mercury in fifteen hours, but the residual metal contained some tin. A second test showed that if the air used is first passed through fuming hydrochloric acid all the tin is removed in twelve hours. A. R. P.

Critical Constants of Mercury. SOPHUS WEBER (*Onnes Comm. Leiden Suppl.*, 1920, 21—31; from *Chem. Zentr.*, 1921, iii, 769—770).—Observation on the critical temperature of mercury showed that it is higher than formerly supposed and probably exceeds 1700° Abs. From a consideration of the data of Bender on the densities of liquid and vaporous mercury, the author shows that the critical temperature must be about 1450+273° Abs. On this assumption, the critical density, d_c, is 5·0 and the critical pressure, p_c, about 1042 atmospheres, which values are in good agreement with those obtained by extrapolation by Knudsen's formula. Plotting d/d_c against T/T_c, and log p_c/p against $(T_c/T-1)$, mercury is shown to fall into line with other monatomic gases.
G. W. R.

Double Nitrate of Aluminium and Potassium. N. M. LAPORTE (U.S. Pat. 1377081).—A double nitrate of aluminium and potassium of the formula $Al(NO_3)_3,3KNO_3,10H_2O$ is prepared by crystallisation from a solution of potassium nitrate and aluminium nitrate in nitric acid. The proportions of the potassium nitrate and aluminium nitrate may be somewhat varied.
CHEMICAL ABSTRACTS.

Graphitisation in Iron–Carbon Alloys. KÔTARÔ HONDA and TAKEJIRÔ MURAKAMI (*Sci. Rep. Tohoku Imp. Univ.*, 1921, **10**, 273—303).—Graphitisation occurs in iron–carbon alloys as a decomposition of cementite and not as a separation of graphite in the molten state. The decomposition is effected catalytically by carbon monoxide or dioxide according to the equations $2CO=CO_2+C$ and $CO_2+Fe_3C=2CO+3Fe$. The process continues until the concentration of the gas in the alloy is reduced below a certain amount or until the temperature falls below the graphitising range. Any treatment of the alloy tending to eliminate carbon dioxide or monoxide present, such as heating above 1400°, will also prevent graphitisation. The formation of flaky graphite is explained by the aggregation of graphite particles as they separate from cementite by reason of interfacial tension. A phase diagram of the system iron–carbon is given embodying the authors' theories.
G. W. R.

The Preparation of Nickel Carbonyl. E. TASSILLY, H. PÉNAU, and E. ROUX (*Bull. Soc. chim.*, 1921, [iv], **29**, 862—864).—In the preparation of nickel carbonyl by passing carbon monoxide over reduced nickel the optimum temperature is 45° at a pressure of 3 cm. Within reasonable limits, the yield of carbonyl from carbon monoxide was independent of the rate of flow of the gas, provided that the velocity was not so great as to prevent condensation by suitable cooling. The coefficient of utilisation was 84% for the metal and 37% for the gas. W. G.

Physico-chemical Analysis of Zirconium Oxychlorides and Zirconium Oxide Sols. MONA ADOLF and WOLFGANG PAULI (*Kolloid Zeitsch.*, 1921, **29**, 173—184; cf. A., 1917, ii, 563).—The complex ionisation of zirconium oxychloride has been examined from experimental data on the hydrogen- and chlorine-ion concentrations, the total zirconium and chlorine concentrations of the solution, the electrical conductivity at 25°, the depression of the freezing point, and the electric migration. The solutions used were made in cold water and kept for ten days before use. The ionisation occurs according to the scheme (i) $ZrAn_4+4H_2O \rightleftarrows Zr(OH)_4+4HAn$, (ii) $2ZrAn_4 \rightleftarrows ZrAn_4,ZrAn_2^{\cdot\cdot}+2An'$, (iii) $2ZrAn_4 \rightleftarrows ZrAn_6''+ZrAn_2^{\cdot\cdot}$(An—an univalent anion). The results show that the ratio between the zirconium hydroxide formed and the unhydrolysed oxychloride is simple and can be expressed in different concentrations by the figures 1 : 1, 3 : 4, 2 : 3, and 1 : 2. A comparison of the hydrolysis with a normal hydrolysis shows that an astonishingly large amount of zirconium hydroxide is formed and a very high degree of hydrolysis is attained. The hydrolysis is not only abnormal in respect of its high value, but also in its connexion with the concentration of the hydrochloric acid. It does not increase with successive dilution, but fluctuates irregularly. It fluctuates between 35% and 49% for a dilution of 500 times. This behaviour is attributed to the formation of complexes, of the type $xZr(OH)_4,yZrOCl_2$, which react with the hydrochloric acid and form highly complex acids of the types $Zr(OH)_4Cl_2H_2$ and $Zr(OH)_2Cl_4H_2$. Curves representing the change in concentration of the hydrogen and chlorine ions respectively present an unique phenomenon, inasmuch as they intersect three times with changing concentration. The points of intersection lie approximately at $N/100$, $N/8$, and $3N/8$. Transport measurements show that the nature of the ion containing zirconium changes in the regions between the intersections of the curves. Tables of the complexes present and the ions to which they give rise are included in the paper. Zirconium oxide sols, produced by the dialysis of solutions of the oxychloride, have been examined. The sols are coagulated by electrolytes only in concentrated solutions ($N/4$ and above). Two of the sols have been investigated and shown to have the composition (*a*) $5Zr(OH)_4,ZrOCl_2$, and (*b*), $7Zr(OH)_4,ZrOCl_2$.

J. F. S.

Mineralogical Chemistry.

Crystal Structure of Alabandite (MnS). RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1921, [v], **2**, 239—249).—The various possible space-groups suggested by the measurements of the *X*-ray reflections from a cube-face and also from the powdered mineral are discussed. The arrangement of the atoms (with either four

or thirty-two chemical molecules to the unit cell) is either that of the "rock-salt type" or a grouping (tetrahedral or tetartohedral) very close to this. L. J. S.

Dolomite from Binn, Switzerland. PAUL KOLLER (*Jahrb. Min.*, 1918, *Beil.-Bd.* **42**, 457—498).—A detailed crystallographic description is given of the colourless water-clear crystals from the saccharoidal dolomite-rock. Crystals of another type from the same occurrence are transparent with a pale yellowish tinge; these have refractive indices $\omega=1\cdot6799$, $\epsilon=1\cdot5013$ (Na), and gave analyses I and II by P. POOTH.

	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	Sp. gr.
I	53·38	46·45	0·13	2·882
II	53·19	46·52	0·09	—
III	52·35	46·02	1·79	2·887

Both these analyses show a slight excess of magnesia over that required by normal dolomite, I corresponding to $32CaCO_3,33MgCO_3$ and II to $26CaCO_3,27MgCO_3$. Corresponding with the low percentage of iron, the refractive indices are lower than any previously determined for dolomite. Analysis III is of dolomite from Scaleglia, Disentis, corresponding with $FeCO_3,36CaCO_3,37MgCO_3$. Etching experiments were made on cleavage flakes with sulphuric, nitric, hydrochloric, acetic, and formic acids, each of which produces different forms of etch-figures. Different forms of etch-figures are also produced by the same acid when of different concentrations. The material of analyses I and II yielded the same type of etch-figures, but the more ferruginous dolomite is rather more readily attacked. L. J. S.

Lazulite from Graves Mountain, Georgia. THOMAS L. WATSON (*J. Washington Acad. Sci.*, 1921, **11**, 386—391).—Analysis, by J. W. WATSON, of material from this well-known locality for lazulite gave:

P_2O_5.	Al_2O_3.	FeO.	MgO.	CaO.	H_2O.	SiO_2.	Total.	Sp. gr.
38·25	33·92	3·99	9·08	3·12	5·83	6·05	100·24	2·958

Deducting silica as quartz, this gives the usual formula $(Fe,Mg,Ca)O,Al_2O_3,P_2O_5,H_2O$. The calcium is, however, higher than previously recorded for the mineral, and this variety is therefore distinguished as calcium lazulite. Other occurrences of lazulite in the United States are noted. L. J. S.

Cornetite from Bwana Mkubwa, Northern Rhodesia. A. HUTCHINSON and A. M. MACGREGOR (*Min. Mag.*, 1921, **19**, 225—232).—The mineral occurs as a thin, crystalline crust of a fine peacock-blue colour on sandstone and shale. The minute crystals are orthorhombic with the forms $m(110)$, $d(102)$, $v(221)$; $a:b:c=0\cdot9855:1:0\cdot7591$. Optic axial plane (001), acute negative bisectrix perpendicular to (100). d 4·10, H 4—5. Analysis gave:

CuO.	Fe_2O_3.	P_2O_5.	H_2O.*	Insol.	Total.
67·28	0·53	18·83	8·24	4·03	98·91

* Loss at 190°, 0·18; loss on ignition 8·77%.

This gives the formula $2Cu_3(PO_4)_2,7Cu(OH)_2$ or perhaps $Cu_3(PO_4)_2,3Cu(OH)_2$. The mineral agrees in its crystallographic and optical characters with cornetite from Katanga (A., 1920, ii, 441) and differs only in not containing cobalt replacing copper.

L. J. S.

Jurupaite, a New Mineral. ARTHUR S. EAKLE (*Amer. Min.*, 1921, **6**, 107—109).—This is another of the several hydrated calcium silicates described from the metamorphic limestone at Crestmore, California (A., 1919, ii, 113). It resembles pectolite in appearance, and occurs in the blue calcite as compact spheres of soft, silky, radiating fibres. The oblique optical extinction suggests monoclinic symmetry. The mineral fuses readily to a clear white glass, and is easily soluble in dilute hydrochloric acid without gelatinisation. It gives no colour with phenolphthalein. The mean of two analyses is:

SiO_2.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
48·87	38·66	4·19	7·89	99·61	2·75

This gives the ratios $2(Ca,Mg)O,2SiO_2,H_2O$. The loss of water at 120° is less than 1% and all is not expelled over the bunsen flame. The formula is therefore written $H_2(Ca,Mg)_2Si_2O_7$, being like crestmoreite and riversideite a derivative of orthosilicic acid. Plazolite (A., 1921, ii, 270) from this locality shows several points of similarity to calcium-garnet. L. J. S.

The Cerium Minerals of Bastnäs, Sweden. PER GEIJER (*Sveriges Geol. Undersökning*, 1921, *Årbok*, **14** (for 1920), No. 6, 1—24).—Cerite, the mineral in which cerium was discovered, is known only from this locality. A detailed description is given of the mode of occurrence of the cerium ore. Examined in thin sections under the microscope, it is seen to consist of a fine grained aggregate of the cerium minerals cerite, bastnäsite, törnebohmite, orthite, fluocerite, and lanthanite, the optical characters of each of which are given. A new estimation of water in the orthite (*d* 4·20) gave 1·52. Introducing this value in Cleve's analysis (1863) the ratios $H_2O:RO:R_2O_3:SiO_2$ become 1 : 4·29 : 2·61 : 5·93, which is a closer approach to the epidote formula. The new mineral *törnebohmite* was detected in the micro-sections as pale green grains (*d* 4·94) differing in optical characters from the associated cerite. Analysis by R. MAUZELIUS gave (also chalcopyrite 0·96, molybdenite not det., insoluble 0·95):

SiO_2.	Ce_2O_3.	$(La,Di)_2O_3$.	Al_2O_3.	FeO.	MnO.	MgO.	CaO.	F.	Ign.	Total.
22·05	27·52	34·85	8·55	1·91	0·05	0·49	0·23	0·29	1·70	99·55

Calculating RO as R_2O_3, these results give a formula, $R_2(ROH)(SiO_4)_2$, analogous to those of andalusite and topaz. The mineral is, however, more closely allied to cerite, from which it differs chemically in containing more aluminium and less calcium. L. J. S.

Monticellite Crystals from a Steel-works Mixer Slag. A. F. HALLIMOND, with analysis by J. H. WHITELEY (*Min. Mag.*, 1921, **19**, 193—195).—The pale-brown, transparent crystals are

orthorhombic with the forms $b(010)$, $m(110)$, and $k(021)$; $a:b:c=0.4382:1:0.5779$. The optic axial plane is parallel to (001) and the acute negative bisectrix perpendicular to (010); α 1·663, β 1·674, γ 1·680; $2V$ 74½°, d 3·20. Analysis shows the presence of 16·5 mol.% of true olivine in solid solution with the monticellite $Ca(Mg,Fe,Mn)SiO_4$, which is in accord with the variation in the physical characters from those of pure monticellite.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	P_2O_5.	CaS.	Total.
34·80	0·24	0·27	trace	4·11	13·39	17·65	28·45	0·905	0·055	99·87

L. J. S.

Chemical Constitution of Zeolites. G. Tschermak (*Sitzungsber. Akad. Wiss. Wien*, 1917, **126**, 541—606, 1918, **127**, 177—289; from *Jahrb. Min.*, 1921, ii, Ref. 150—153).—Twenty-one new analyses are given of various zeolites. In all cases the ratio $Al:Ca(Sr,Ba)+Na_2(K_2)$ is 2 : 1. Omitting oxygen, all zeolites may be represented by the formulæ $Si_xAl_2CaH_{2y}$ and $Si_zAl_2Na_2H_{2v}$, where x and z range from 2 to 10, and y and v from 2 to 9. Or again, neglecting hydrogen, they all contain a group $Si_2Al_2CaO_8$ or $Si_2Al_2Na_2O_8$. This group is regarded as a nucleus ("Kern") and represented as *Kc* or *Kn* respectively (also *Kb* and *Ks* for the corresponding barium and strontium nuclei). The various zeolites are regarded as compounds of one or other of these nuclei with a silicic acid, combined water, and water of crystallisation. The silicic acid and water of hydration are supposed to form a network enclosing the nuclei. Such a structure is regarded as offering an explanation of the variation of the optical characters of the zeolites with loss or gain of water, the various adsorption phenomena, and the ease with which the bases may be replaced. The following is a summary of the different groups:

A. Orthosilicates in combination with SiH_4 and H_2O: Natrolite, $SiH_4Kn=Si_3Al_2Na_2H_4O_{12}$. Scolecite, $SiH_4KcOH_2=Si_3Al_2CaH_6O_{13}$. Mesolite, a double salt of these two in the ratio 1 : 2. Edingtonite, $SiH_4KbOH_2,aq=Si_3Al_2BaH_8O_{14}$. Gismondine, $H_2OKcO_2H_4,aq=Si_2Al_2CaH_8O_{12}$, also with SiH_4 in place of H_2O. Laumontite, $SiH_4KcSiH_2=Si_4Al_2CaH_8O_{16}$. Thomsonite, a double salt of the compounds H_2OKnOH_2,aq and H_2OKcOH_2 in the ratio 1 : 3; also in the latter SiH_4 in place of H_2O.

B. Disilicates combined with polysilicic acids and H_2O: Analcite, $Si_2H_4Kn=Si_4Al_2Na_2H_4O_{12}$, also with Si_4H_8, Si_4H_4, or H_2O in place of Si_2H_4. Faujasite, $Si_4H_8KcO_2H_4,4aq$, also with Si_2H_4. Chabazite, $Si_2H_4KcO_2H_4,2aq=Si_4Al_2CaH_{12}O_{18}$, also with Si_4H_8, Si_2H_2, or SiH_4. Gmelinite with *Kn* in place of *Kc*. Levynite like chabazite with Si_2H_2 and SiH_2. Stilbite, $Si_4H_8KcOH_2,2aq=Si_6Al_2CaH_{14}O_{23}$, also with Si_6H_{12}, Si_4H_4, or Si_2H_4. Harmotome with *Kb* instead of *Kc*. Phillipsite like stilbite but with Si_2H_4, Si_2H_2, SiH_4, SiH_2. Heulandite, $Si_4H_4KcO_2H_4,aq=Si_6Al_2CaH_{10}O_{21}$, also with Si_6H_6, Si_4H_8, or Si_2H_4. Brewsterite with *Ks* in place of *Kc*. Mordenite like heulandite with Si_3H_8. L. J. S.

Ferroanthophyllite from Idaho. Earl V. Shannon (*Proc U.S. Nat. Museum*, 1921, **59**, 397—401).—A greyish-green, asbesti-

form mineral intergrown with galena occurs in the Tamarack-Custer mine near Gem in the Coeur d'Alene district. It is orthorhombic with optically positive elongation, $\alpha=1{\cdot}668$, $\gamma=1{\cdot}685$; *d* 3·24. It is insoluble in acids, and fuses to a black, magnetic glass. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	$H_2O(<110°)$.	$H_2O(>110°)$.	Total.
49·30	1·30	2·15	30·50	3·48	10·73	0·66	0·18	2·13	100·43

Deducting ferric oxide and alumina as gedrite (RO,R_2O_3,SiO_2), this gives the metasilicate formula ($(Fe,Ca,H_2,Mn)O,SiO_2$), but only when the water, which is expelled at a high temperature, is taken into account. Being the iron end-member of the anthophyllite series the name ferroanthophyllite is applied [cf. iron-anthophyllite, A., 1919, ii, 165]; similarly, the magnesium end-member of this series may be called magnesioanthophyllite. L. J. S.

A New Type of Mineral Water: Nitrated Waters. CHARLES LEPIERRE (*Compt. rend.*, 1921, **173**, 783—786).—A mineral water found at Ericeira in Portugal, obtained from a well 15 metres deep and 50 metres from the sea, contained 0·686 gram of nitrates, expressed as sodium and calcium nitrates, per litre, equivalent to 18·8% of the total mineral salts. Their origins are considered to be due to biochemical and hydrological phenomena. W. G.

Analytical Chemistry.

Apparatus for Technical Gas Analysis. G. ANDOYER (*Ann. Chim. anal.*, 1921, **3**, 293—294).—The apparatus consists of a measuring burette provided with a water-jacket; the bottom of the burette is connected with a levelling reservoir, whilst the top is fitted with a three-way tap. The absorption pipettes are connected, in turn, with the stem of the tap and thence with the burette; the other branch of the three-way tap carries a small funnel by which water may be introduced for washing out reagents.

W. P. S.

Atmospheric Corrections for the Harcourt Standard Pentane Lamp. E. B. ROSA, E. C. CRITTENDEN, and A. H. TAYLOR (*J. Opt. Soc. Amer.*, 1921, **5**, [v], 444—452).—A review of results obtained for the factor correcting the candle-power of the Harcourt 10-candle pentane lamp for variations of humidity of the atmosphere. The mean correcting factor determined at the National Physical Laboratory is 0·645, whilst the result obtained at the Bureau of Standards is 0·567, the factor in each case representing the percentage decrease in candle-power due to an increase of 1 litre of water vapour per cub. metre of air. The discrepancy in the two values is traced to a difference of atmospheric temperature in the two cases, and it is shown that the experimental values are

brought into agreement by using two factors, namely, a factor 0·52% decrease in candle-power per litre of water vapour per cub. metre of air (in the absence of any temperature difference) and a factor 0·08% decrease per degree rise of temperature. The factor 0·52% agrees with the recently determined value found at the Bureau of Standards and is in agreement with results obtained recently by Takatsu and Tanaka in Japan. It is suggested that 15° should be taken as the normal atmospheric temperature for calculation of the candle-power of the lamp. J. S. G. T.

Device for Filling Burettes. G. BRUHNS (*Chem. Zeit.*, 1921, **45**, 1004).—The lower end of a burette, without a tap, is connected with a short vertical length of glass tube carrying a side tube; this side tube is bent downwards and provided with a jet and spring clip. The end of the vertical tube is connected by a rubber tube with a piece of glass tube which reaches to the bottom of the reservoir containing the reagent solution. The burette is filled by opening a spring clip on the latter piece of rubber tube and applying suction to the top of the burette. W. P. S.

Colorimetric Method of Estimating Hydrogen-ion Concentration. Some Applications in the Analytical Laboratory. NORMAN EVERS (*Analyst*, 1921, **46**, 393—400).—The colorimetric method is described in detail; the method depends on the fact that with different indicators the colour change extends over a characteristic zone of hydrogen-ion concentration. The method may be used with clear or turbid liquids free from colour, for coloured liquids, and is useful for ascertaining the reaction of such substances as sodium salicylate, morphine hydrochloride, calcium chloride, potassium iodide, etc. W. P. S.

Methyl-orange as an Indicator in the Presence of Indigo Carmine. FRANK X. MOERK (*Amer. J. Pharm.*, 1921, **93**, 675—679; cf. A., 1907, ii, 910).—The sensitiveness of methyl-orange, particularly in slightly coloured solutions, may be increased by the addition of indigo-carmine; 1 gram of methyl-orange and 2 to 4 grams of indigo-carmine per litre of water is a suitable concentration for the indicator solution. W. P. S.

A Simple Method for the Preparation of Sodium Hydroxide Solution free from Carbonate. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1413—1417).—Commercial sodium hydroxide is dissolved in water to form an approximately normal solution. To each litre 50 c.c. of milk of lime is added; after well shaking, the solid is allowed to settle and the caustic solution decanted off with the usual precautions. The solution is titrated and diluted to $0{\cdot}1N$; it is quite free from carbonate, and contains only 1—2 mg. of calcium per litre, which has no influence in analytical determinations. S. I. L.

Direct Estimation of Water in Mixed Sulphuric and Nitric Acids. E. BERL and W. VON BOLTENSTERN (*Zeitsch. angew. Chem.*, 1921, **34**, 526—528).—A calorimeter for determining the heat of dilution of the sample consists of a vacuum-lined vessel

40 mm. in diameter and 300 mm. high. It is fitted with an agitator consisting of two blades of sheet glass or aluminium connected together and worked by two rods, and with a thermometer graduated to 1/10 of a degree. Two hundred c.c. of distilled water are placed in the calorimeter, 20 c.c. of mixed acid added through a fine glass tube dipping below the surface of the water, and the corrected rise of temperature obtained as with the Mehler bomb calorimeter. The water content of the acid is read off from a curve prepared by a series of tests of different dilutions of an acid of known composition. Different ratios between the two acids correspond with different curves. An increase of 1% in the N_2O_3 content of the acid was also found to give a water figure 1% too high. Organic matter is without effect, and for varying dilutions of a mixture of constant composition determinations can be rapidly made to an accuracy of 0·05—0·06% H_2O. C. I.

A New Process for the Estimation of Fluorine in the Cold. TRAVERS (*Compt. rend.*, 1921, **173**, 836—838).—The fluorine is first converted by suitable means into alkali fluoride. To the fluoride solution, generally alkaline, a known amount of silica, as potassium silicate, is added. Usually twice the theoretical amount of silica required to convert the fluorine to potassium silicofluoride is sufficient. The liquid is then neutralised with hydrochloric acid, using methyl-orange as an indicator, and an excess of acid, about 2 c.c., is added. Solid potassium chloride is added until the solution contains 20% of it. The precipitate is filtered off, washed free from acid with 20% potassium chloride and titrated with *N*/5-potassium hydroxide as previously described in the estimation of silica (this vol., ii, 710). One c.c. of *N*/5-potassium hydroxide is equivalent to 0·0057 gram of fluorine. W. G.

Estimation of Small Quantities of Fluorine in Natural Products by Means of Hempel and Scheffler's Gasometric Method. H. SERTZ (*Zeitsch. anal. Chem.*, 1921, **60**, 321—330).—The method described by Hempel and Scheffler (A., 1899, ii, 380) is suitable for the estimation of the small quantities of fluorine occurring in certain vegetable substances; when the ash of the latter contains much carbonate or chloride, a preliminary treatment with 10% acetic acid is recommended. W. P. S.

Some Notes on the Estimation of Sulphur and Chlorine by the Lamp Method. S. BOWMAN (*J. Inst. Petroleum Tech.*, 1921, **7**, 334—338).—In estimating sulphur in petroleum products by this method a certain amount of sulphur is always absorbed by the wick. A method of eliminating this source of error is described. [See further *J. Soc. Chem. Ind.*, 1921, Dec.] L. A. C.

Estimation of Sulphate-, Chloride-, and Carbonate-ions in Soda-Lime-Glass. MASAO IKAWA (*J. Chem. Soc. Japan*), 1921, **42**, 768—785).—The sulphate and chloride radicles are precipitated as barium sulphate and silver chloride respectively, from the clear solution, obtained by warming on a water-bath the finely-powdered

glass with three times its weight of pure ammonium hydrogen fluoride in presence of acid with constant stirring. The sulphur in the glass is estimated by oxidation with bromine water in the course of the decomposition of a sample with ammonium hydrogen fluoride, followed by precipitation as barium sulphate, the amount of sulphur being calculated from the difference between this and the estimation of the sulphate. For the determination of the carbonate, the sample is decomposed with 30% solution of the fluoride in a lead flask, and the carbon dioxide produced absorbed in soda-lime as in the Fresenius-Classen method.

Finely powdered glass absorbs 0·1260% of carbon dioxide by exposure to the air for eight months, but the absorption during the preparation of the sample for analysis is negligible.

Pure ammonium hydrogen fluoride is prepared by passing silicon fluoride into water and treating the hydrofluorosilicic acid formed with excess of ammonia. The solution is filtered and concentrated in a platinum dish; ammonium hydrogen fluoride crystallises on cooling; it is further purified by sublimation. A 30% solution of ammonium hydrogen fluoride is not decomposed by heating at 90°, but in more concentrated solutions decomposition occurs, a 50% solution evolving hydrogen fluoride, ammonia, and ammonium fluoride at that temperature. K. K.

Rapid Process for Estimating Phosphoric Acid. H. COPAUX (*Compt. rend.*, 1921, **173**, 656—658).—The method is based on the fact that when phosphoric acid in the presence of another acid, such as sulphuric or hydrochloric acid, is shaken with ether and an alkali molybdate the phosphomolybdic acid formed unites with ether and water to give a dense yellow liquid which is not miscible with water. The estimation is conducted in a specially designed graduated tube, which is described. Into the tube is run 10 c.c. of the phosphate solution, 10 c.c. of 20% sulphuric acid, and sufficient ether to give a layer of 3—4 mm., and the contents are mixed. To the mixture is added in five or six portions 15 c.c. of a solution of sodium molybdate containing 100 grams of molybdic anhydride per litre, the mixture being shaken after each addition. The tube is then spun in a centrifuge and when the separation of the three liquid phases is complete, the volume of the dense yellow liquid is read. The tube having been previously calibrated against a standard solution of a phosphate, the percentage of phosphoric anhydride in the solution under examination can at once be determined. If the solution contains citric acid or citrates, these must be removed by preliminary evaporation and ignition.

W. G.

Estimation of Phosphates in Waters. DANIEL FLORENTIN (*Ann. Chim. anal.*, 1921, **3**, 295—296).—The colorimetric method described depends on the production of a blue colour when a dilute phosphoric acid solution is treated with ammonium molybdate in sulphuric acid solution and a small quantity of stannous chloride. Ten c.c. of the water to be tested are treated with two or three drops of molybdate reagent (100 c.c. of 10% ammonium molybdate

solution mixed with 300 c.c. of 50% sulphuric acid) and one drop of stannous chloride solution (0·1 gram of tin dissolved in 2 c.c. of hydrochloric acid and diluted to 10 c.c.). As little as 0·01 mg. of P_2O_5 per litre yields a distinct blue coloration, the intensity of which reaches a maximum in ten minutes. Comparison with the colorations given by known amounts of phosphoric acid gives the quantity of the latter present in the test solution. W. P. S.

Detection of Pyrophosphoric Acid in the Presence of Orthophosphoric Acid and Metaphosphoric Acid. D. BALAREFF (*Zeitsch. anal. Chem.*, 1921, **60**, 385—392).—To detect pyrophosphoric acid in the presence of orthophosphoric acid, the solution containing the two acids is rendered slightly alkaline towards phenolphthalein, treated with a few drops of 5% copper sulphate solution and dilute acetic acid is added until the precipitate is just dissolved; a minute crystal of copper pyrophosphate is then introduced. A precipitate of copper pyrophosphate forms gradually. Another portion of the neutralised solution may be treated with silver nitrate and acetic acid; the latter dissolves the yellow silver orthophosphate, whilst the white pyrophosphate remains insoluble. If metaphosphoric acid is also present, the precipitate obtained with copper or silver salts must be further examined, since certain forms of metaphosphoric acid yield precipitates resembling those given by pyrophosphate. For this purpose, the precipitate is dissolved in nitric acid, the solution neutralised, then acidified with acetic acid, and tested with albumin solution for the presence of metaphosphoric acid. The reaction described by Berthelot and Andre (A., 1897, ii, 158, 283) is untrustworthy in the presence of metaphosphoric acid. W. P. S.

Detection of some Metals and of Arsenic in Plant and Human Organs. A. KEILHOLZ (*Pharm. Weekblad*, 1921, **58**, 1482—1495).—The methods available for the detection of minute quantities of arsenic, copper, manganese, zinc, aluminium, and lithium have been examined, and a scheme has been drawn up and applied to the examination of the organs of the human body and of plants for these elements. The organic matter is destroyed by means of sulphuric and nitric acids, these are removed in the usual manner, and the residue is taken up in water.

Forty per cent. of the solution is examined for arsenic, 20% for lithium, and the remainder for copper, manganese, and zinc, which are removed in succession, the solution being finally examined for aluminium.

The Bloemendal modification of Marsh's apparatus was selected for the arsenic examination, the mirrors obtained being dissolved in excess of chromic acid, the excess being titrated with iodine. The arsenic in the mirror can also be determined by Ramberg's method, which depends on the reaction $As+5I+4H_2O=H_3AsO_4+5HI$; this is more suitable for exact determination of very small quantities, but requires a mechanical shaking apparatus. In the examination of urine it was found that organic arsenic compounds, such as cacodyl derivatives, are not destroyed by the ordinary

acid combustion; the permanganate method gives accurate results in these cases.

Copper is best determined electrolytically, using a platinum cathode in a platinum crucible, which serves as anode, a potential difference of 2 volts, and a current of 4—8 milliamperes. At 60—70°, two to four hours are required. The anode is weighed on a Kühlmann balance. Zinc and manganese do not interfere.

Manganese can be determined colorimetrically by Marshall's method (A., 1901, ii, 350) or electrolytically precipitated as peroxide. Zinc is best determined electrolytically in acetic acid solution in the cold. Aluminium is estimated colorimetrically with alizarin (Atack, A., 1915, ii, 842) and lithium spectroscopically.

Application of the methods worked out showed arsenic to be present sometimes in the liver, generally in urine, and in all the plants examined; copper and zinc generally in the liver, and in some plants; manganese in the liver, brains, and blood, and in some plants; aluminium was not found in human organs, but lithium was present in nearly every organ examined, and in all the plants. Tabulated results are given in milligrams of each element per kilogram of material examined. S. I. L.

New Type of Combustion Bomb made of Krupp's Special Steel. W. A. Roth, R. Macheleidt, and Irmg. Wilms (*Zeitsch. angew. Chem.*, 1921, **34**, 537—538).—A new calorimeter combustion bomb designed to replace the usual type with platinised or enamelled interior is constructed of Krupp's special acid-resisting "V_2A" steel (20—23% Cr, 6—9% Ni, 0·1—0·3% C). The bomb, which is made of either the "Langbein" or "Kroeker" type, is provided with a quartz or porcelain dish in which the substance to be burnt is placed. This is suspended in the interior of the bomb, from two hooks in the electric leads. The insulated lead is a rod of the chrome nickel steel, and the other is a tube serving for the admission of oxygen and the egress of the gases from the combustion, and is made of silver, since a small bent tube cannot yet be constructed out of the steel alloy. The bomb can be used for the combustion of all ordinary organic substances, including nitro-compounds, but it is not available for substances containing halogens or a high percentage of sulphur, the alloy not being resistant to nascent sulphuric or halogen acids. Normally, with the former category of organic compounds, including coals with 5—7% of sulphur, only about 0·2 mg. of iron is dissolved, and no nickel. This would generate approximately 0·2 cal. With the latter class of substances several mg. of both iron and nickel are dissolved from the surface of the metal. The susceptibility to attack, however, appears to grow less with use, and substances with a comparatively high sulphur content can then be successfully burnt. G. F. M.

The Determination of the Degree of Oxidation of Coals. Georges Charpy and Gaston Decorps (*Compt. rend.*, 1921, **173**, 807—811).—The oxidation of coal may take place in two ways. In the first, there is direct fixation of oxygen with a resulting increase in total weight and volatile matter. In the second, there

is simple oxidation with formation of carbon dioxide and water and a consequent diminution in total weight and a slight decrease in the percentage of volatile matter. The first reaction is the more important at low temperatures. The method proposed for determining the degree of oxidation of a sample of coal consists in powdering and sifting the coal and heating a known weight of it with 50% sodium hydroxide solution at 100° for two hours, using 10 c.c. of the solution for each gram of coal. The resulting liquid is diluted and filtered, the filtrate being acidified with sulphuric acid and made up to a known volume. To an aliquot portion an excess of standard potassium permanganate solution is added and the mixture is left at the ordinary temperature for two hours, after which the excess of permanganate is titrated back. In this way is determined the oxidation index, that is the number of grams of oxygen necessary to oxidise the organic matter dissolved by the sodium hydroxide from one kilo. of coal. Coals required to produce a resistant coke should, as a rule, have an oxidation index not exceeding 2. Curves are given showing the variation with time of the oxidation index and total weight of two samples of coal kept at 150°. W. G.

Apparatus for the Estimation of Carbon Dioxide (in Carbonates). WILHELM KOHEN (*Chem. Zeit.*, 1921, **45**, 1027).—The apparatus consists of a small reaction flask provided with a tapped funnel for the introduction of the acid; the neck of the flask is fitted with a small reflux condenser of the ball type, and this is connected with a sulphuric acid bulb and a potash bulb. The contents of the flask may be boiled to expel the last traces of carbon dioxide, the condenser and sulphuric acid bulb preventing any water vapour entering the potash bulb. W. P. S.

A New Method of Estimating Silica. TRAVERS (*Compt. rend.*, 1921, **173**, 714—717).—The silica is first converted into an alkali silicate and to it, in solution in a silver dish, is added at least 1 gram of potassium fluoride for every 0·15 gram of silica. Hydrochloric acid is added until the liquid is just neutral, and then a further 2 c.c. are added, and finally 7—10 grams of potassium chloride for every 50 c.c. of liquid. The precipitated potassium silicofluoride is collected on a hardened filter in an ebonite funnel and washed with a 20% solution of potassium chloride until free from acid. The wet precipitate is suspended in boiling water and titrated with $N/5$-potassium hydroxide, free from carbonate, using phenolphthalein as indicator. One c.c. of the alkali corresponds with 0·005 gram of silica. Details are given for the application of the method to the estimation of traces of silica in alkali hydroxides and salts, to the analysis of quartz and silicates, and to the estimation of silica in the presence of fluorine and aluminium. W. G.

Gravimetric Estimation of Potassium by the Cobalt Method. A. VÜRTHEIM (*Rec. trav. chim.*, 1921, **40**, 593—599).—A study of the conditions under which a precipitate of constant composition is given by potassium compounds with a cobalt salt

and sodium nitrite. Such a precipitate, apart from variations in water content, can be obtained: these variations are eliminated by drying at 110° to constant weight. The method is thus rendered of use for direct estimation. H. J. E.

Estimation of Potassium in Soils and Fertilisers. HARALD R. CHRISTENSEN and NIELS FEILBERG (*Landw. Versuchs.-Stat.*, 1921, **97**, 27—56).—The cobaltinitrite method of Mitscherlich (A., 1912, ii, 204, 996) is modified, whereby 5 c.c. of saturated sodium chloride solution are added together with the precipitating reagent, thereby ensuring more complete precipitation. The method is applicable to the estimation of potassium in fertilisers and soil extracts. [See further *J. Soc. Chem. Ind.*, 1921, 820A.] G. W. R.

The Acidimetric Estimation of Ammonium Salts with Formalin. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1463—1469).—Formaldehyde reacts readily with ammonium salts in aqueous solution, forming hexamethylenetetramine and setting free the acid originally combined with the ammonia. The procedures of Gaillot (A., 1913, ii, 240) and of van Bers (A., 1917, ii, 578) have been found unsatisfactory. Very accurate results are obtained by adding 5 c.c. of formalin (B.P., neutral to phenolphthalein) to 25 c.c. of the solution (about 0·1 mol. per litre) of ammonium salt, and titrating the liberated acid after one minute with $N/10$-sodium hydroxide solution. It is equally satisfactory to use excess of soda with the formalin, titrating the excess with acid after fifteen minutes.

The sodium hydroxide must be free from carbonate, and the water used for the solutions free from carbon dioxide; phenolphthalein is used as indicator. Small quantities of neutral salts do not interfere. The method is not suitable for the accurate estimation of formaldehyde. S. I. L.

Chemical Analysis with Membrane Filters. II. Volumetric Estimation of Zinc. GERHART JANDER and HANS CAESAR STUHLMANN (*Zeitsch. anal. Chem.*, 1921, **60**, 289—321; cf. A., 1919, ii, 520).—The collection and washing of zinc sulphide precipitates are facilitated by the use of membrane filters; the sulphide should be precipitated from an acetic acid solution containing sodium acetate. Of volumetric methods for the estimation of zinc sulphide, Mann's method (decomposition of the zinc sulphide with moist silver chloride and subsequent titration of the zinc chloride) and acidimetric methods are trustworthy. W. P. S.

Sensitive Reaction for Copper. P. FALCIOLA (*Giorn. Chim. Ind. Applic.*, 1921, **3**, 354—355).—Cupric salts may be detected in solution even in 0·00001 N-concentration, by means of alkali thiocyanate solution mixed with cold saturated gallic acid solution, a decided turbidity being produced. The cupric solution should be neutral and free from silver, lead, and bismuth. Similar precipitation of copper occurs if the gallic acid in the reagent is replaced by tannic acid, catechol, or quinol, but not by resorcinol. [Cf. *J. Soc. Chem. Ind.*, 1921, Dec.] T. H. P.

Rapid Electro-analysis of Brass. A. LASSIEUR and (MME) A. LASSIEUR (*Compt. rend.*, 1921, **173**, 772—775).—The following details of working should be strictly adhered to. 0·5 Gram of brass in the form of thin foil is dissolved in 20 c.c. of sulphuric acid (50% by weight) and 1 c.c. of nitric acid (*d* 1·33), the liquid being heated to boiling at first. When solution is complete, the liquid is diluted to 70 c.c. with water and electrolysed, using a current of 4—5 amperes and rotating electrodes. The operation lasts forty minutes, during which the whole of the copper is deposited and the nitric acid is completely reduced. To the liquid, freed from copper and containing the rinsings of the electrodes, are added 25 c.c. of sodium hydroxide (*d* 1·33), 15 c.c. of glacial acetic acid, and 10 c.c. of a saturated solution of sodium fluoride in the order named. The liquid is cooled to the ordinary temperature and electrolysed, the zinc being deposited on a copper-coated cathode, using a current of 4 amperes. In some cases, at the end of the first electrolysis a slight deposition of zinc is noted. This zinc at once dissolves again when the current is stopped. W. G.

The Separation of Aluminium from Glucinum. II. HUBERT T. S. BRITTON (*Analyst*, 1921, **46**, 437—445; cf. this vol., ii, 657).—Aluminium cannot be separated from glucinum satisfactorily by means of ammonium carbonate in either hot or cold solutions, as not only does the precipitated aluminium hydroxide carry down considerable amounts of glucina, but much alumina remains in the ammonium carbonate solution. Treatment of a solution of the two metals with ammonium sulphite yielded, on boiling, a precipitate containing all the aluminium and much glucinum, although the latter alone gives no precipitate with the reagent. Separation by means of sodium hydrogen carbonate (Parsons and Barnes, A., 1907, ii, 52) yields satisfactory results if neither the glucinum nor aluminium in 100 c.c. of the solution saturated with sodium hydrogen carbonate exceeds 0·15 gram, and if the adsorption in both precipitations is kept at a minimum by vigorous stirring. A. R. P.

Reaction of Manganese, Iron, and Cobalt. D. BALAREFF (*Zeitsch. anal. Chem.*, 1921, **60**, 392—393).—The precipitate containing manganese and iron hydroxides is washed, dissolved in nitric acid, the solution boiled to oxidise ferrous salt, then neutralised with sodium hydroxide solution, treated with silver nitrate solution, and then rendered ammoniacal or acidified with acetic acid; in the presence of as little as 0·2 mg. of manganese per litre, a black precipitate is observed in the ammoniacal solution, or a yellowish-brown precipitate in the acetic acid solutiou. Cobalt and ferrous salts yield a similar reaction. W. P. S.

Titrations with Potassium Permanganate. ANT. JILEK (*Chem. Listy*, 1921, **15**, 105—109, 138—140).—The titration of sodium oxalate, oxalic acid, ferrous ammonium sulphate, and electrolytic iron (prepared according either to Treadwell or Classen) was studied. The results of these titrations agreed with each other more closely if the volumes of 0·1*N*-potassium permanganate used

were approximately equal. Treadwell's method did not require a control estimation. Standardisation against sodium oxalate, oxalic acid, and ferrous ammonium sulphate is very facile and accurate. Classen's method was rapid and accurate, if the iron dissolved in sulphuric acid is titrated in the presence of platinum. Solutions of 0·1*N*-ferrous sulphate, slightly acidified with sulphuric acid, and exposed to air, are practically unaffected after twenty-four to forty-eight hours. There is practically no danger of the oxidation of these solutions during their filtration through paper or glass wool.

CHEMICAL ABSTRACTS.

Volumetric Estimation of Mixtures of Permanganate, Dichromate, and Chromic Salts. NITYA GOPAL CHATTERJI (*Chem. News*, 1921, **123**, 232—233).—The method depends on the fact that permanganate is converted into hydrated manganese dioxide by treatment with a solution containing manganese sulphate and zinc sulphate, whilst dichromate is not affected. Titration of a mixture of permanganate and dichromate with ferrous sulphate solution before and after such treatment gives a measure of the amounts of the two substances present. The estimation of chromium salts is based on their oxidation to dichromate by heating with hydrated manganese dioxide in dilute sulphuric acid solution.

W. P. S.

The Iodometric Determination of Iron. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1510—1522).—The slowness of the reaction between ferric salts and iodides is found to be due to the hydrolysis of the former, resulting in the formation of colloidal ferric hydroxide. Strong acids accelerate the reaction, but not if present in excess, since complex ferric salts are formed. The reaction is very suitable for analytical work if the iron solution be about *M*/10, and the correction concentration of acid and iodide be obtained. For 25 c.c. of iron solution, about 2 c.c. of concentrated hydrochloric acid (25—39%) and 1·6 grams of potassium iodide are required; after fifteen minutes, the iodine is titrated with thiosulphate. Sulphates and oxalates interfere; phosphates interfere only if the solution is not sufficiently acidic. Even ferric solutions as dilute as 0·001 *M* can be accurately titrated in *N*/10-hydrochloric acid solution if sufficient iodide (0·5 gram for 10 c.c. of iron solution) be used. S. I. L.

The Different Methods of Attack of Ochreous Minerals. A. RAYNAUD (*Bull. Soc. chim.*, 1921, [iv], **29**, 905—910).—For the analysis of the ochres, 0·5 gram of the finely-powdered mineral, previously dried at 100—105°, is weighed into a platinum crucible, strongly ignited for a few minutes, and weighed again. The loss in weight is due to water of combination and traces of carbonate and organic matter. To the residue 4—5 c.c. of dilute sulphuric acid and 8—10 c.c. of fuming hydrofluoric acid are added, and the mixture is evaporated to dryness at a gentle heat, finally heated more strongly until fuming has ceased, and then ignited. The residue, which consists of oxides of iron and alumina, is weighed,

the loss in weight by the acid treatment being reckoned as silica. The residue is fused with potassium hydrogen sulphate, and after rapid cooling the fused mass is extracted with water, the iron reduced to the ferrous state, and estimated by titration with permanganate. The percentage of aluminium oxide is got by difference from the mixed oxides. The process is rapid and gives results quite comparable with those obtained with more complicated methods. W. G.

Application of Amalgams in Volumetric Analyses. II. Estimation of Vanadium and Uranium. TAMAKI NAKAZONO (*J. Chem. Soc. Japan*, 1921, **42**, 761—768; cf. this vol., ii, 596).—Vanadium can be titrated with potassium permanganate either by reduction to (*a*) the bivalent state by shaking with liquid zinc amalgam for three minutes in the absence of air in the manner previously described (*loc. cit.*), or (*b*) to the quadrivalent state by treatment with saturated silver sulphate solution, after shaking with zinc amalgam for three seconds only.

Uranium is titrated with potassium permanganate after reduction to the quadrivalent state by shaking with zinc amalgam for thirty seconds in the presence of air. K. K.

Estimation of Fermentation Glycerol. KARL FLEISCHER (*Zeitsch. anal. Chem.*, 1921, **60**, 330—338).—One hundred c.c. of the glycerol solution (obtained by the fermentation process) is distilled under reduced pressure with superheated steam, the temperature of the distillation flask being raised gradually to 250°; the distillate is collected in a flask immersed in a water-bath at 70°. This receiving flask is provided with a reflux apparatus supplied with a current of water at 70°, and the top of the reflux apparatus is connected with an ordinary condenser, receiver, and pump. When glycerol ceases to collect in the flask, the steam supply is cut off, and the contents of the flask are heated at 100° under reduced pressure until practically all water has been removed; a small current of air is admitted to the flask through a capillary to aid in the removal of the water. The residue of glycerol in the flask is then weighed; its specific gravity is determined so that an allowance can be made for the small quantity of water still present. W. P. S.

Sugar Calculations. J. F. LIVERSEEGE (*Analyst*, 1921, **46**, 446—450).—Equations are given for correcting the specific rotatory power of a sugar or mixture of sugars for temperature and concentration and examples are given of the method of calculating the proportions of the various commercial sugars in solutions from the observed specific rotatory power before and after inversion, the value of K (that is, reduction expressed as dextrose and lævulose) before and after fermentation, and the total organic solids. A table of constants and factors for the more important sugars is also given. A. R. P.

Estimation of the Pentose Sugars. HERMAN AUGUSTUS SPOEHR (*Carnegie Inst. Pub.*, 1919, No. **287**, 36—37).—The hexose sugars

are fermented with baker's yeast, and the alcohol and other products of fermentation are removed by distillation. The residual solution containing pentoses is then caused to react with hot Fehling solution, and the cuprous oxide obtained by reduction is estimated by an iodometric titration. The non-fermentable sugar must be recognised as pentose by the proper tests. CHEMICAL ABSTRACTS.

The Quantitative Estimation of Dextrose and Lævulose in a Solution. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1921, **118**, 120—128).—The optical rotation of the solution, and the total reducing power on copper sulphate by Pflüger's method (*Pflüger's Archiv*, 1906, **114**, 242) for dextrose are determined. Pflüger's table of reducing powers of dextrose in terms of cuprous oxide is used as the standard of reference for dextrose, and an analogous table is experimentally determined for lævulose. Knowing the optical rotation of dextrose and lævulose separately, the content of dextrose and of lævulose is determined graphically or by simple calculation. H. K.

Comparative Estimations of Lignin in Cellulose. E. HEUSER and G. WENZEL (*Papierfabr.*, 1921, **19**, 1177—1184).—The degree of accuracy of a number of methods for the estimation of lignin has been compared using a sample of unbleached, rasped Mitscherlich sulphite-cellulose, which gave the qualitative reactions for lignin distinctly, with a total solid content of 91·5%, benzene–alcohol extract (resin and fat) 1·48%, and ash 0·85%. The estimation of lignin by Becker's modification (*Papierfabr.*, 1919, **17**, 1325) of König and Rump's method (*Zeitsch. Unters. Nahr. Genussm.*, 1914, **28**, 184) using 72% sulphuric acid, gives too high results, owing to the separation on dilution of colloidal products which contain no lignin, but are weighed as such. Too high results are also obtained by König and Becker's modification (*Papierfabr.*, 1919, **17**, 565) of Krull's method (*Diss.*, *Danzig.*, 1916, 19) using gaseous hydrogen chloride, and König and Rump's method (*loc. cit.*) using dilute hydrochloric acid under pressure, owing to the incomplete saccharification of the cellulose. On the other hand, trustworthy determinations of lignin in cellulose are obtained by a modification of Willstätter and Zechmeister's method (A., 1913, i, 955), in which 1 gram of the sample is covered with 70 c.c. of 41·4% hydrochloric acid in a stoppered flask, frequently shaken during eighteen hours, diluted with ten times the volume of water, and boiled for ten minutes. F. M. R.

Estimation of Lactic Acid in Blood. G. A. HARROP, jun. (*Proc. Soc. Expt. Biol. Med.*, 1920, **17**, 126—133).—The method is based on Denigès's observation that lactic acid is converted by concentrated sulphuric acid into acetaldehyde, and can be estimated with phenols and morphine alkaloids. Five c.c. of blood or serum are heated for 4—5 minutes on a water-bath with 15 c.c. of acidified copper sulphate solution, and excess of powdered calcium hydroxide is added to the cold liquid. After thirty minutes, it is filtered, and one part of the filtrate is added to four parts of concentrated sulphuric acid while the mixture is being shaken and cooled in water

at 0°. After being placed in a boiling-water bath for two minutes, it is again cooled to 0°, three drops of a 5% solution of guaiacol are added, and after keeping for twenty minutes the rose colour which has developed is compared with standards similarly prepared.

CHEMICAL ABSTRACTS.

A Modification of Aschman's Method of Determining the Iodine Value. B. M. MARGOSCHES and R. BARU (*Chem. Umschau*, 1921, **28**, 229—232 and 245—247).—The iodine monochloride solution is prepared as follows: 15 grams of potassium iodide are dissolved in 50 c.c. of water and chlorine is passed through until the iodine at first precipitated is completely redissolved. The solution is left for five hours, and is then decanted from the crystalline precipitate, which is washed, and the solution and washings are made up to 500 c.c. with water. The solution is even more stable than Wijs's solution.

0·5—0·1 Gram of the oil or fat (according to the iodine value expected) is taken and dissolved in 10 c.c. of carbon tetrachloride and 10 c.c. of the iodine monochloride solution are added. The mixture is shaken and it is essential that the shaking is repeated two or three times during the first half of the absorption period, which varies from two to four hours for fats, six hours for non-drying, eight hours for semi-drying, and twenty-four hours for drying oils when only 60% excess of iodine is used. The time can be reduced by using a larger excess (75%) when six to eight hours are sufficient even for drying oils. The excess of iodine is titrated in the usual way. An iodine monochloride solution of half the above concentration can be used equally well. The values obtained usually lie between the corresponding Hübl and Wijs values. H. C. R.

A Modified Babcock Method for Determining Fat in Butter. N. W. HEPBURN (*Cornell Univ. Agric. Exp. Sta., Memoir* 37, 669—690).—The size of the bottle used in the Babcock cream test is modified to suit the fat estimation in butter. A 23 cm. bottle is used for 9 gram samples and a 15 cm. for 6 gram samples, the diameter of the graduated part of the neck being 9·07 and 9·04 mm. respectively for the two sizes. With the former, the semi-solid butter is covered with 9 c.c. of lukewarm water, and 17·6 c.c. of commercial sulphuric acid are added slowly and with vigorous shaking, followed by more water to bring the liquid to the graduation marks. After five minutes' centrifuging, more water is added to bring the liquid again to the graduations. The bottle is again centrifuged for four minutes and placed in a water-bath at 52—54°, and the volume of fat is read off. Glymol may be used to flatten the meniscus. The results obtained compare favourably with those from chemical analyses. The accuracy is the same with both sizes of bottle, but the 23 cm. is more easily manipulated. A. G. P.

The Estimation of Enols by Hieber's Copper Acetate Method. W. DIECKMANN (*Ber.*, 1921, **54**, [*B*], 2251—2254; cf. Hieber, this vol., ii, 466).—Hieber's method for the estimation of enols is not valid, since it depends on the assumption that the com-

plex copper salts of the latter are not affected under the experimental conditions (in alcohol–chloroform solution in the presence of an equimolecular amount of copper acetate) by an equivalent amount of acetic acid. This is true only of the copper salts of strongly acidic enols, for example, α-mesityloxideoxalic ester, but not of those derived from ethyl acetoacetate and similar substances of a more feebly acidic nature. Repetition of Hieber's experiment with "equilibrium ethyl acetoacetate" or with a specimen containing a larger proportion of enol leads to the formation of about 7·5% of the copper salt which is produced to the extent of about 11% when the quantity of copper acetate is doubled, and about 14% when the quantity is quadrupled. The reaction between ethyl acetoacetate and copper acetate does not depend on the combination of the enolic form, but on the attainment of an equilibrium between the copper compound of ethyl acetoacetate, copper acetate, and acetic acid, which, in consequence of the rapid keto-enolic transformation, is independent of the enol content of the ethyl acetoacetate. The coincidence of Hieber's datum with the known enolic content of "equilibrium ethyl acetoacetate" is purely accidental and depends on the experimental conditions and relative quantities of material; the remarkable agreement shown in other instances is doubtless conditioned by the fact that, in accordance with Classen's rule, acidity and tendency towards enolisation are, in general, parallel characteristics. The copper salts of other enols show an analogous but gradually differing behaviour from that of the compound derived from ethyl acetoacetate. The figures enclosed within the brackets represent the percentages of the substances which remain unchanged after treatment with two molecular proportions of acetic acid and one of copper acetate in alcohol–chloroform solution: ethyl copper benzoylacetate (*ca.* 38), copper acetylacetone (60), ethyl copper oxalacetate (*ca.* 85), copper benzoylacetone (*ca.* 100), methyl copper α-mesityloxide oxalate (*ca.* 100).

Hieber's method is applicable only in the few cases in which the copper salt is not attacked by acetic acid and the rate of keto-enolic transformation is so small that an alteration of the enolic content does not occur during the course of the experiment. H. W.

Estimation of Citronellol and Citronellal by Formylation. C. T. Bennett (*Perf. and Essent. Oil Rec.*, 1921, **12**, 351).—The formic acid method for the estimation of citronellol and citronellal is absolutely untrustworthy. Even with pure citronellol, the results were high when 100% acid was used, and low with a weaker acid, and in the case of mixtures, such as otto of rose, the results are vitiated by the action of the acid on the geraniol present, which it partly converts into formate. The action of 100% formic acid on citronellol yields a mixture of products containing unchanged citronellol, a small amount of what is probably an aliphatic or cyclic terpene, citronellol formate, b. p. 99—100°/7 mm., the *compound* $OH\cdot CMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CH_2\cdot O\cdot CHO$, b. p. 129°/5 mm. d=0·9651, μ=1·4488, α=1° 46″, and the corresponding *diformate*, b. p. 140—141°/7 mm. G. F. M.

The Acid Amide Fraction of the Nitrogen of Peat. E. J. MILLER and C. S. ROBINSON (*Soil Sci.*, 1921, **11**, 457—467).—It is shown that both glutamic acid and aspartic acid are obtainable from peat by hydrolysis with hydrochloric acid. Attempts to separate glutamic acid directly from the hydrolysate were not successful. The application of Foreman's method (cf. A., 1914, ii, 826) in a slightly modified form resulted in the separation of both glutamic and aspartic acids, and in the estimation of pyrolidonecarboxylic acid from the hydrolysate. W. G.

Estimation of Cyanides Iodometrically with the aid of Benzene. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1921, **42**, 454—462).—Benzene can be used as an indicator in iodometry for the accurate estimation of cyanides. The original solution is mixed with 1% boric acid solution, then with the same quantity of 1% borax solution, and titrated; or impurities in the original solution are removed by addition of sodium hydrogen carbonate and after neutralisation with hydrochloric acid, the titration is performed. In each case, benzene is added to indicate the end point; when the benzene is tinged, sodium hydrogen carbonate is added, and the titration continued. The method is applicable in general iodometry, when the sample is coloured strongly or contains precipitates. The method has been used in analysing samples of potassium chromate and potassium ferricyanide. K. K.

Estimation of Thiocyanate in the Presence of Salts which Precipitate Silver Nitrate. ANDRÉ DUBOSC (*Ann. Chim. anal.*, 1921, **3**, 297—298).—To estimate thiocyanate in the presence of chlorides, etc., the sulphur in the thiocyanate is oxidised to sulphate and then precipitated as barium sulphate. The oxidation is best made with a reagent prepared by electrolysing a mixture of sodium chloride and magnesium chloride solutions; this reagent should contain 2% of "active" chlorine. A suitable quantity of the thiocyanate is dissolved in 50 c.c. of water, 50 c.c. of 4% barium chloride solution and 50 c.c. of the reagent are added, and, after ten minutes, the mixture is acidified with 10 c.c. of hydrochloric acid, boiled, and the barium sulphate collected and weighed. W. P. S.

The Estimation of Creatinine in the Presence of Acetone and Acetoacetic Acid. NATHAN F. BLAU (*J. Biol. Chem.*, 1921, **48**, 105—118).—The author demonstrates, by numerous analyses, the disturbing effects of the presence of acetone substances on the estimation of creatinine by the method of Folin. He describes a method of removing these interfering substances from urine by boiling, the temperature being kept low by the addition of methyl alcohol. C. R. H.

Estimation of the Alkaloid Content of Lupines. F. MACH and P. LEDERLE (*Landw. Versuchs.-Stat.*, 1921, **98**, 117—124).—The authors discuss the errors which may occur in the estimation of the alkaloid content of lupines by extraction with chloroform–ether and precipitation of the alkaloids by silicotungstic acid. Calculation of the alkaloid content from the weight of residue

obtained by ignition of the alkaloid–silico-tungstate precipitate is inexact because alkaloids of varying molecular weight occur in different species of lupines. In the method recommended, 15 grams of lupine meal are extracted by shaking with 100 c.c. of ether, 50 c.c. of chloroform, and 10 c.c. of 15% sodium hydroxide solution. After keeping, the ethereal layer is filtered and an aliquot part is diluted with an equal volume of ether and washed three times with 20 c.c. of 1% hydrochloric acid. The ether and chloroform are removed by evaporation and the alkaloids precipitated by 10 c.c. of 10% silicotungstic acid. The precipitate is collected in a Gooch crucible, washed with 1% hydrochloric acid, dried at 120° to constant weight, and ignited. In the case of yellow lupines, where the principal alkaloid is lupinine, the factor 0·2475 is used for calculating the amount of alkaloid from the weight of the ignited residue. For lupanine, occurring in other species, the factor 0·1744 is used. The amount of alkaloids may also be calculated from the loss on ignition of the dried precipitate. G. W. R.

Colour Reaction for Nicotine and Coniine. JUAN A. SANCHEZ (*Semana med.*, **28**, 61—64; from *Chem. Zentr.*, 1921, iv, 559).—One drop of a solution of nicotine or coniine gives on shaking with 5 c.c. of a solution of 0·5 gram of vanillin in 100 c.c. of strong hydrochloric acid a coloration varying from rose red to deep cherry red, according to the concentration. The reaction is given also by indole and scatole, but not by pyridine. The solutions, examined spectroscopically, show two bands in the green (λ 525 and 490) and one in the violet. G. W. R.

Estimation of Tannin. JOHN ARTHUR WILSON and ERWIN J. KERN (*J. Ind. Eng. Chem.*, 1921, **13**, 772—774).—Two grams of hide powder, washed previously with water, extracted with chloroform, and dried, are placed in a bottle, 100 c.c. of the tannin solution (of such concentration that the 2 grams of hide powder are more than sufficient to remove the tannin) are added, and the mixture is shaken for six hours. The mixture is then filtered through fine filter-cloth arranged in a tubular funnel and the tanned hide powder is washed by passing a slow stream of water through the funnel for about twelve hours, or until the wash water no longer gives a coloration with ferric chloride solution. The hide powder is dried in the open air for twelve hours, then for two hours in a vacuum oven, and weighed. The increase in weight represents the amount of tannin in 100 c.c. of solution.
W. P. S.

Application of the Laws of Chemical Kinetics to Quantitative Analysis. Fractional Estimation of Tannins in General and Tannins of Wine in Particular. J. CLARENS (*Bull. Soc. chim.*, 1921, [iv], **29**, 837—852).—The method is based on the fact that the oxygen absorption by tannins in wine when plotted against time indicates the presence of at least four different substances. Taking into account the oxygen absorption results and the results obtained by oxidation with potassium permanganate, the author outlines a method for calculating the relative amounts of the

different types of tannins present in a mixture such as occurs in wines. W. G.

A Possible Source of Error in Testing for Bence-Jones Protein. C. W. MILLER and J. E. SWEET (*J. Biol. Chem.*, 1921, **48**, 21—22).—Attention is directed to the danger of confusion, under certain conditions, in testing urine for Bence-Jones protein, owing to the presence of protein digestion products, and also to emulsions formed with preservative toluene. C. R. H.

Necessity for Exact Hæmoglobin Estimations and Erythrocyte [Red Corpuscle] Counts. K. BÜRKER (*Münch. med. Woch.*, 1921, **68**, 571—573; from *Chem. Zentr.*, 1921, iv, 319—320). —The author recommends absolute estimation of hæmoglobin in blood on account of the untrustworthiness of colour index determinations. A special apparatus is devised for the estimation, whereby diluted blood after reduction with sodium thiosulphate is compared colorimetrically with a standard hæmoglobin solution. Estimations of hæmoglobin content and erythrocyte counts with the blood of certain domestic animals showed that, although the absolute values vary, the amount of hæmoglobin per unit corpuscular surface is approximately constant from one species to another. G. W. R.

The Gold Number of Commercial Gelatins. FELIX A. ELLIOTT and S. E. SHEPPARD (*J. Ind. Eng. Chem.*, 1921, **13**, 699—700).—The gold number expresses the number of mg. of colloid necessary to prevent the precipitation of 10 c.c. of standard gold solution by 1 c.c. of 10% sodium chloride solution. It is shown that the gold number decreases with decrease in the concentration of the gelatin solution, and that the number increases the longer the gelatin solution is kept after it has been made. There is but little difference in the protective action of various commercial gelatins, and the gold number does not bear any simple relation to those properties of chief interest to users of gelatins. W. P. S.

Analysis of Shepherd's Purse (*Capsella bursa pastoris*). CLEMENS GRIMME (*Pharm. Zentr.-h.*, 1921, **62**, 495—499).—Estimation of the choline and acetylcholine by precipitation with alcoholic platinum chloride solution yields trustworthy results if the sample is treated previously with alcohol to precipitate and remove gum-resins (cf. Boruttau and Cappenberg, this vol., i, 487). A liquid extract of good quality should contain 14% of total solids, 3% of mineral matter, and yield at least 5% of platinum precipitate corresponding with 2·15% of choline compounds. W. P. S.

Analysis of Shepherd's Purse (*Capsella bursa pastoris*). H. CAPPENBERG (*Pharm. Zentr.-h.*, 1921, **62**, 560—562).—The method described by Grimme (preceding abstract) is an improvement on the original process, but the author points out that the value of liquid extract of *Capsella bursa pastoris* does not depend on the quantity of choline compounds present, since the extract contains other active principles. W. P. S.

INDEX TO PATENTS.

ERRATA.

Vol. 112 (Abstr., 1917).

Page	Line	
ii. 167	14	*for* "hydrogen" *read* "hydrogen sulphide."

Vol. 118 (Abstr., 1920).

Page	Line	
ii. 308	5*	*for* "$3H_2PO_4$" *read* "$3H_3PO_4$."
ii. 737	5 6	,, "**Ethyl Benzoate**" *read* "**Benzyl Benzoate.**"
	8 14 19	,, "ethyl benzoate" *read* "benzyl benzoate."
ii. 753	20	*after* "GARNER" *insert* "FREDERICK CHALLENGER."

Vol. 120 (Abstr., 1921).

Page	Line	
i. 62	10	*for* "**Triquinonylmethanes**" *read* "**Triquinolylmethanes.**"
	11	,, "**Tri-2-quinonylmethane**" *read* "**Tri-2-quinolylmethane.**"
 i. 63 	14 5 7	,, "triquinonylmethane" *read* "triquinolylmethane."
	8	,, "*triquinonylcarbinol*" read "*triquinolylcarbinol.*"
i. 165	25	,, "ZEIGLER" *read* "ZIEGLER."
i. 258	14	,, "nitrate" *read* "nitrite."
i. 266	2	,, "793,794" *read* "i, 793,794."
i. 330	19*	,, "GORDON" *read* "CORDON."
i. 384	9 10	,, "*Arch. Anat. Physiol.*" read "*Virchow's Archiv.*"
i. 388	2	,, "*Soil. Sci.*, **172**," read "*Soil. Sci.*, **11**."
i. 503	2	,, "HALFTEN" *read* "HAEFTEN."
i. 511	26	,, "fluoreneoxalate" *read* "fluoreneglyoxylate."
i. 516	24	,, "**Osindole**" *read* "**Oxindole.**"
i. 566	20*	,, "M. E. FOURNEAU" *read* "E. FOURNEAU."
i. 702	26	,, "vitamin-*A*" *read* "vitamin-*B*."
i. 751	8	,, "twice" *read* "half."
i. 796	16*	,, "ethyl *r*-pinate" *read* "ethyl *r*-pinonate."
i. 914	8	,, "F. R. JONES" *read* "F. R. JONES and W. B. TISDALE."
ii. 6	13	,, "*N*-ethyl" *read* "NEt_2."
ii. 176	10*	,, "JOSEPH" *read* "JOSEF."
ii. 191	9	,, "boron" *read* "baron."
ii. 224	12*	,, "*Zeitsch. anal. Chem.*" read "*Zeitsch. angew. Chem.*"
ii. 285	14*	,, "Thompson" *read* "Thomson."
ii. 285	9*	,, "THOMPSON" *read* "THOMSON."
ii. 344	13*	,, "KOLFTHOF" *read* "KOLTHOFF."
ii. 573	3	,, "BARBOROVSKÝ" *read* "BABOROVSKÝ."
,,	4	,, "HANÁK" *read* "HANÁKOVA."
ii. 621	21*	,, "**103**" *read* "**100.**"

ii. 811, col. ii, entries under "**Rüggli**" should be under "**Ruggli**" on ii, 812.

* From bottom.